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Rheological Properties of Poly(1,3-dimethyl-1-butenylene) and Model Atactic Polypropylene

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ABSTRACT: A series of atactic polypropylene polymers were prepared by anionic polymerization of 2-methyl-1,3-pentadiene followed by saturation with hydrogen. The polymers were nearly monodisperse in molecular weight distribution and covered a wide range of molecular weights. Measurements before and after hydrogenation were used to establish the molecular weight and temperature dependence of rheological properties. When the results were compared with data on commercial isotactic polypropylene it was found that the viscosities of the two types of polymers are essentially the same. Hence the materials that were synthesized proved to be useful model polymers for studying the physical properties of polypropylene in the liquid state. Results on the frequency dependence of the dynamic shear moduli are reported including measurement of the plateau modulus, G_N, and the steady-state compliance, J_e°. The data were also used to estimate the monomeric friction factor, ζ.

Introduction

Polypropylene (PP) is a common thermoplastic polymer. It can be synthesized with different stereochemical constitutions, or tacticities, by changing the type of catalyst used for polymerization. The two types that are most important commercially are isotactic and atactic. The former is a semicrystalline polymer having a melting point near 170 °C[2] whereas the latter is an amorphous polymer that remains in the liquid state until it vitrifies near 0 °C.

Propylene polymerization catalysts also strongly influence the molecular weight distribution, generally producing polymers that are very polydisperse. Most of the rheological studies on polypropylene have been done with samples having a broad molecular weight distribution.[3–7] Interpreting the data obtained in these experiments could be simplified if narrow molecular weight distribution polymers were available.

We have recently reported a method for preparing atactic polypropylene that is essentially monodisperse in molecular weight.[8] It consists of first polymerizing 2-methyl-1,3-pentadiene with an organolithium catalyst. The resulting polymer contains only 1,4-addition structures (cis and trans). Saturating the residual double bonds with hydrogen yields an atactic polymer with ideal Bernoullian statistics.[8] A series of these polymers with molecular weights from 4.4×10^4 to 3.8×10^5 were prepared and used to establish the viscosity–molecular weight relationship and the temperature dependence of viscoelastic properties as well as other parameters such as the monomeric friction factor and the molecular weight between entanglements. Similar information was obtained for the unsaturated precursor polymer, poly(1,3-dimethyl-1-butenylene), PDMB.[8,9]

When our results are compared with data on commercial isotactic polymers, we find that viscosity of the two polymers at equal weight average molecular weight is essentially the same. Hence atactic polymers prepared in the manner described here represent useful model materials for studying the physical properties of polypropylene in the liquid state.

This report covers only linear homopolymers. However, the anionic polymerization techniques used to make these materials could also be used to make branched polymers with precise structures and block polymers of propylene with other monomers.[10] Such materials would be uniquely valuable because they cannot be made with conventional propylene polymerization catalysts.

Experimental Section

Polymer Synthesis. Anionic polymerization was used to prepare the precursor polymer from (*E*)-2-methyl-1,3-pentadiene. The method consisted of adding *sec*-butyllithium as an initiator to a 10–40% v/v solution of the purified monomer in benzene. The reaction was allowed to proceed at 40 °C for 5 days to 2 weeks to ensure complete conversion. Termination was done by adding degassed methanol. The resulting polymer was precipitated from the polymerization solvent with methanol, dried, and then redissolved in cyclohexane. Hydrogenation was carried out with a catalyst system (Pd on $CaCO_3$) and under reaction conditions similar to those described by Rachupudy et al.[11] A more detailed explanation of the synthesis procedure is given in ref 8.

Molecular Characterization. NMR measurements on PDMB confirmed earlier reports that it consists entirely of 1,4 addition structures (% 1,4 > 99.4). The ratio of cis to trans double bonds is approximately 60:40. The NMR spectrum of the same polymers after reaction with hydrogen indicates that residual unsaturation was reduced to less than 0.3%.

Polypropylene is one of the few vinyl polymers where the NMR spectrum related to stereochemical sequence distribution has been completely determined up to the heptad level.[12] Using these assignments, we analyzed the methyl triads and pentads and found[8] that the chain sequence statistics conformed to ideal Bernoullian with a probability of meso addition, P_m, of 0.502. We conclude that the polymers are truly atactic and not just amorphous stereoirregular polypropylene that is often called atactic.

Average molecular weights and the molecular weight distribution of all polymers were determined previously by light scattering, osmometry, and size exclusion chromatography.[8] Values of M_w and the ratio M_w/M_n are listed in Table I.

We also determined the intrinsic viscosity of the polypropylene polymers in tetralin at 135 °C (see Table I and Figure 1). A linear regression analysis with these data resulted in the Mark–Houwink–Sakurada parameters shown in the following equation.

$$[\eta] = 1.85 \times 10^{-4}\, M_w^{0.73_7}\ \mathrm{dL/g} \qquad (1)$$

This result is somewhat different than that found by Parrini, Sebastiano, and Messina for isotactic polypropylene ($[\eta] = 9.42 \times 10^{-5} M_w^{0.78_4}$).[13] The discrepancy between the two equations is greatest in the low molecular weight region. For example, Parrini's equation applied to sample B predicts an M_w that is 30% higher than the value found with eq 1. Conversely, generally good agreement is found between eq 1 and that of Moraglio, Gianotti, and Bonicelli ($[\eta] = 1.58 \times 10^{-4} M_n^{0.75_9}$), which is based on atactic samples.[14]

Also listed in Table I are the glass transition temperatures for both polymer series. We note that the average value of the T_g of our atactic polypropylenes is −4.7 °C. This is 6–10 °C higher than the usual values reported[15,16] for atactic polypropylene. We have presented some possible explanations for this difference in

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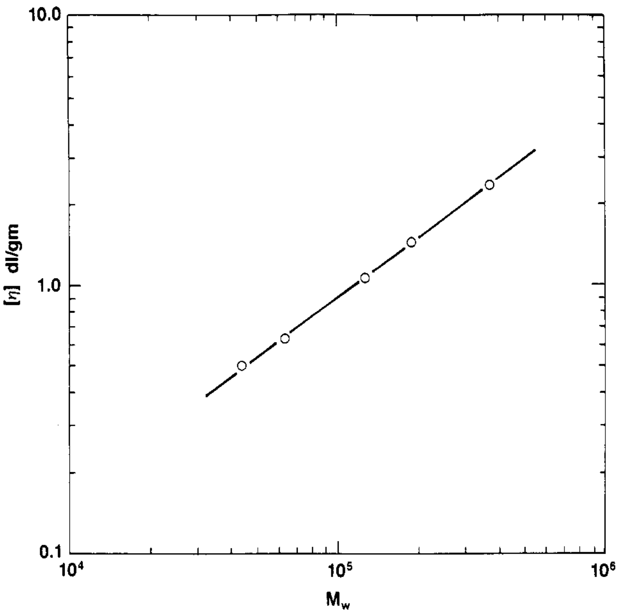

Figure 1. Intrinsic viscosity of atactic polypropylene as a function of M_w in tetralin at 135 °C.

Table I
Molecular Properties of Poly(1,3-dimethyl-1-butenylene) and Polypropylene

PDMB

sample	$10^{-4} M_w$, g/mol	M_w/M_n[a]	$[\eta]_{THF}$,[a] dL/g	T_g, °C
B	4.45	1.07	0.47_2	1.1
D	5.87	1.05	0.59_0	2.2
F	12.5	1.07	1.00_2	2.6
G	19.0	1.13	1.26_8	2.2
H	37.7	1.14	2.18_7	2.3

PP

sample	$10^{-4} M_w$, g/mol	M_w/M_n[a]	$[\eta]_{tetralin}$, dL/g	T_g, °C
B	4.37	1.06	0.50_2	-8.0
D	6.35	1.06	0.63_0	-5.3
F	12.6	1.06	1.04	-4.5
G	18.9	1.12	1.45	-4.2
H	37.1	1.10	2.39	-4.6

[a] Reference 8.

ref 8. Recently, Burfield and Doi[17] have given a value for T_g of -5 °C for essentially atactic (in the Bernoullian sense) material.

The specific gravity of the polymers were determined by weighing them in air and water at 25 °C. From this information we calculated that the density at this temperature is 0.880 g/cm^3 for PDMB and 0.854 g/cm^3 for our atactic PP.

Rheological Characterization. The rheological properties of all polymers were measured with a System 4 rheometer manufactured by Rheometrics, Inc. It was equipped with 25-cm diameter parallel disks and a 1 × 10^4 g cm torque transducer. The dynamic moduli, $G'(\omega)$ and $G''(\omega)$, were determined as a function of frequency, ω, by subjecting the sample to small sinusoidal strains (1-10%). Measurements were performed at temperatures from 25 °C to at least 75 °C and in some cases to 190 °C. The frequency range was sufficiently large so that data were obtained from the high-frequency transition region down to the low-frequency terminal region.

Logarithmic plots of $G'(\omega)$ and $G''(\omega)$ taken at temperature T were superimposed on those for temperature T_r by a translation of log a_T along the frequency axis. No shifts along the modulus axis were required. Time-temperature reduction such as this can be expressed by

$$G^{\dagger}(\omega,T) = G^{\dagger}(\omega a_T,T_r) \tag{2}$$

where the dagger (†) stands for either one prime(′) or two primes (″). For both polymers we chose a reference temperature, T_r, of 75 °C. Figures 2 and 3 show G' and G'' as a function of ωa_T for the model polypropylene polymers; Figures 4 and 5 show similar data for PDMB.

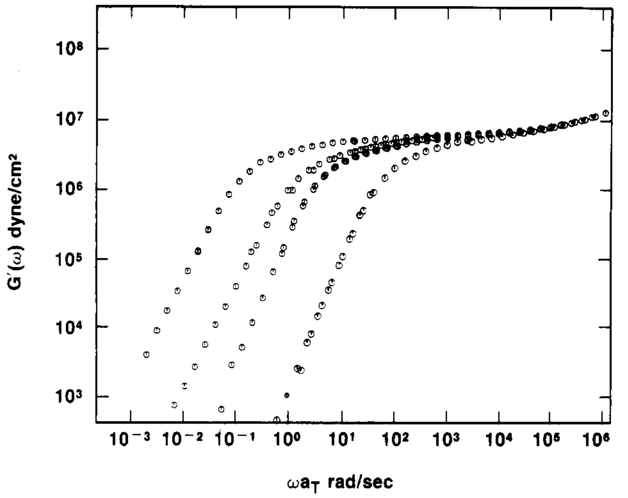

Figure 2. Dynamic storage modulus master curves for atactic PP samples at a reference temperature of 75 °C. Samples D, F, G, and H are shown.

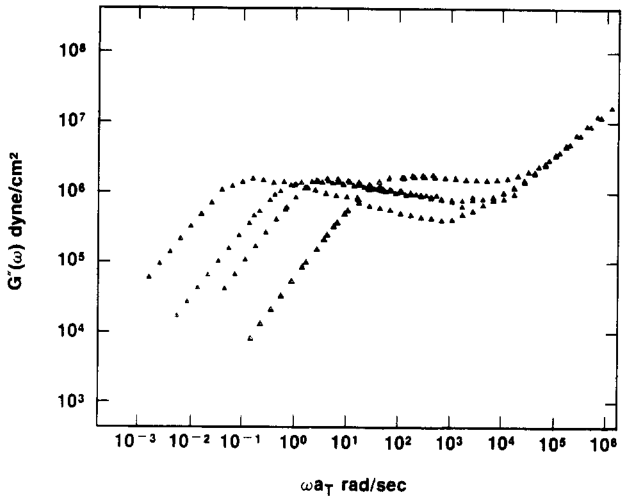

Figure 3. Dynamic loss modulus master curves for atactic PP samples at a reference temperature of 75 °C. Samples D, F, G, and H are shown.

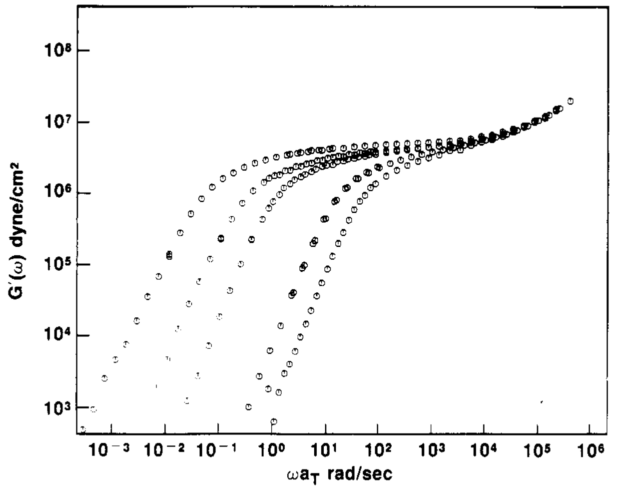

Figure 4. Dynamic storage modulus master curves for all PDMB samples at a reference temperature of 75 °C.

For all polymers the data extend to low enough frequencies so that the viscosity attains a constant value of η_0:

$$\eta_0 = \lim_{\omega\to 0} |\eta^*(\omega)| = \lim_{\omega\to 0} \frac{[G'(\omega)^2 + G''(\omega)^2]^{1/2}}{\omega} \tag{3}$$

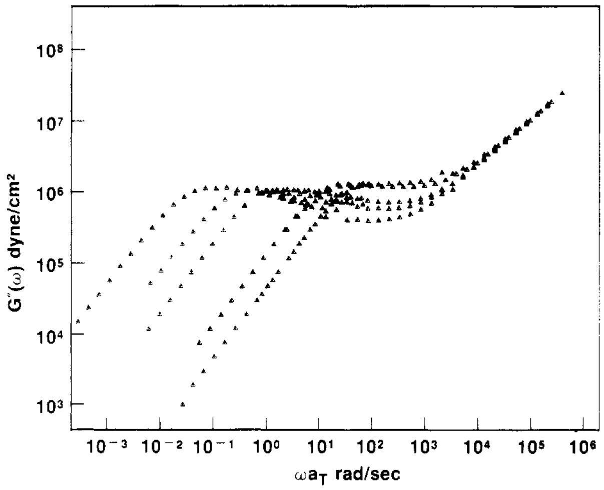

Figure 5. Dynamic loss modulus master curves for all PDMB samples at a reference temperature of 75 °C.

For the three lowest molecular weight polymers in each series, it was also possible to determine the steady-state compliance, $J_e°$, from the region where $J'(\omega)$ became constant:

$$J_e° = \lim_{\omega \to 0} J'(\omega) = \lim_{\omega \to 0} \frac{G'(\omega)}{G'(\omega)^2 + G''(\omega)^2} \qquad (4)$$

Results and Discussion

Temperature Dependence of Viscoelastic Properties. Because of the high melting point of isotactic propylene, liquid-state rheological measurements are confined to a relatively narrow temperature region (190–250 °C) that is also far from the glass transition temperature. Over this limited range viscosity appears to follow an Arrhenius form

$$\log a_T = \eta(T)/\eta(T_r) \propto e^{E_\eta/RT} \qquad (5)$$

with an activation energy, E_η, of approximately 10 kcal/mol.[6,7]

Recently Plazek and Plazek[16] studied the creep compliance of an essentially atactic sample of polypropylene from T_g to T_g + 80 °C. As is found for other polymers,[18] working in a range near T_g shows that the temperature dependence of viscoelastic properties is not Arrhenius-like but instead closely conforms to the Vogel–Fulcher–Tamman–Hesse (VFTH)[16] equation

$$\log a_T = A + B/(T - T_\infty) \qquad (6)$$

The Plazek sample had a T_g of −11 °C[18] while the constants B and T_∞ in eq 6 were 640 and −60 °C.[20]

The samples used in this study have a temperature dependence very similar to the one studied by Plazek. Figure 6 shows a plot of $(T_r - T)/\log a_T$ versus $T - T_r$. The plot is linear in agreement with eq 6, and from the slope and intercept we obtain B = 586 °C and T_∞ = −49 °C. The average T_g of our samples is −4.7 °C. If the temperature shift factors a_T obtained from this study and from the Plazek study are compared by using reference temperatures at equal $T - T_g$ (say 75 and 68.7 °C, respectively), we find that from 25 to 200 °C they differ by no more than 15%.

Equation 6 can also be used to derive an apparent activation energy for viscous flow

$$E_\eta(T) = \mathrm{d} \ln a_T/\mathrm{d}(1/RT) \qquad (7a)$$

$$E_\eta(T) = 2.303[RBT^2/(T - T_0)^2] \qquad (7b)$$

where R is the gas constant. At 200 °C eq 7 gives E_η = 9.7 kcal which is in good agreement with the value cited above.

Temperature shift factors plotted in the same way as in Figure 6 but for the unsaturated polymer PDMB are shown in Figure 7. A linear relationship is also found that corresponds to VFTH parameters B = 583 °C and T_∞ = −44.5 °C. For most polymers the differences between T_g and T_∞ is approximately 50 °C. This result together with the finding that the values of B for the two polymers are essentially identical (586 and 583 °C) assures that their temperature dependence is the same when compared at equal $T - T_g$.

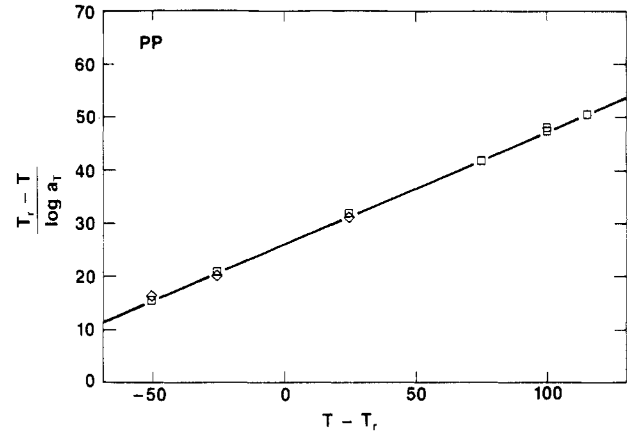

Figure 6. $T_r - T$ divided by log of temperature shift factor for atactic PP. T_r is 75 °C.

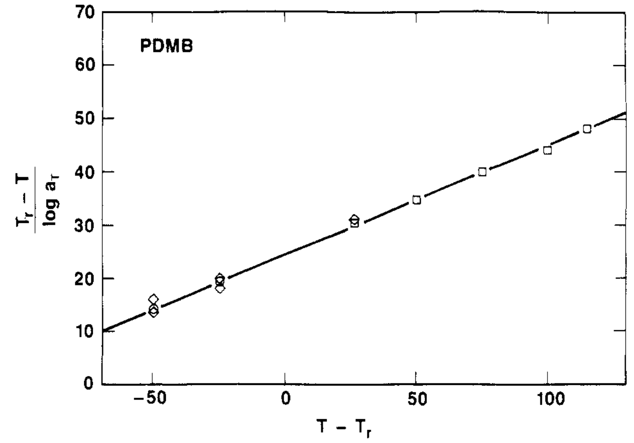

Figure 7. $T_r - T$ divided by log of temperature shift factor for PDMB. T_r is 75 °C.

Plateau Modulus and Recoverable Compliance. The dynamic elastic modulus, $G'(\omega)$, of atactic PP and PDMB are shown in Figures 2 and 4. For both polymers there is an extensive plateau region where the modulus has an essentially constant value (G_N) of about 7 × 10⁶ dyn/cm². A better estimate of G' in this region can be obtained from the following formula which is a form of the Kramers–Kronig relation for determining the real part of G^* in a frequency region above a peak in the imaginary part.[21] (Information on peak height and position of $G''_{\max}$ is given in Table II.)

$$G_N = (2/\pi) \int_{-\infty}^{\infty} G''(\omega) \, \mathrm{d} \ln \omega \qquad (8)$$

Experimental values of $G''(\omega)$ from the highest molecular weight PP and PDMB samples (letter code H) were used for the quadrature indicated by eq 8. For each case it was necessary to extrapolate G'' to zero at high frequencies to separate the terminal response from the adjoining transition region.[22] (See Figure 8, parts a and b.) The values of G_N so obtained were 8.5 × 10⁶ dyn/cm² for atactic PP[23] and 6.3 × 10⁶ dyn/cm² for PDMB. Using the following formula from rubber elasticity theory[24]

$$M_e \equiv \rho RT/G_N \qquad (9)$$

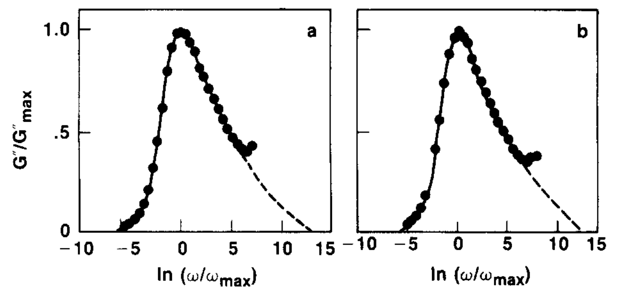

Figure 8. Dynamic loss modulus as a function of ln ω for (a) PP sample H and (b) PDMB sample H. The integral in eq 6 was determined from the area bounded by the experimental data and the dashed-line extrapolation.

Table II
Rheological Properties of Poly(1,3-dimethyl-1-butenylene) and Polypropylene at 75 °C

sample	η_0, P	G''_{max}, dyn/cm^2	ω_{max}, s^{-1}	$J_e°$, cm^2/dyn
		PDMB		
B	3.5×10^4			4.7×10^{-7}
D	1.1×10^5	1.2×10^6		5.0×10^{-7}
F	1.5×10^6	1.1×10^6	2.5	5.6×10^{-7}
G	6.7×10^6	1.1×10^6	1.0	
H	7.5×10^7	1.3×10^6	0.1	
		PP		
B	2.4×10^4			5.5×10^{-7}
D	8.1×10^4	1.7×10^6		4.5×10^{-7}
F	9.9×10^5	1.5×10^6	5.0	4.1×10^{-7}
G	5.4×10^6	1.8×10^6	1.6	
H	4.5×10^7	1.4×10^6	.16	

we estimate that the molecular weight between entanglements is 2.9×10^3 for PP and 4.0×10^3 for PDMB.

It is of interest to compare the effect that saturation has on the plateau modulus of 1,4-diene polymers. PDMB increases by a factor of 1.4. Polybutadiene increases from 1.25×10^7 to 2.2×10^7 dyn/cm^2, a ratio of 1.9.[25] The largest increase is found for polyisoprene where hydrogenation increases G_N from 0.44×10^7 to 1.25×10^7 dyn/cm^2, a ratio of 2.8.[26]

An increase in the plateau modulus is consistent with the Graessley–Edwards correlation[27] which relates G_N to the chain configuration and polymer density. Their formula predicts rather well the increases found for PDMB and polybutadiene. However, it overestimates the plateau modulus of the polyisoprene and underestimates G_N of the hydrogenated material. At present it is not known what factors are responsible for this discrepancy.

The relaxation spectra of entangled linear polymers are usually quite narrow. One criterion for judging spectral width is the ratio of the mean square relaxation time to the square of the mean. The quantity is easily obtained experimentally from the product $J_e°G_N$.

$$J_e°G_N = \langle\tau^2\rangle/\langle\tau\rangle^2 \qquad (10)$$

For the three lowest molecular weight polymers in each series, it was possible to measure $J_e°$ and obtain the following average values (see Table II):

$$J_e° = 5.1 \times 10^{-7} \text{ cm}^2/\text{dyn (PDMB)} \qquad (11)$$

$$J_e° = 4.7 \times 10^{-7} \text{ cm}^2/\text{dyn (PP)} \qquad (12)$$

From these data and the estimates of G_N given above, we find that $J_e°G_N$ is 3.2 for PDMB and 4.0 for PP. These values are larger than those found for polyisoprene and polybutadiene ($J_e°G_N \simeq 2$–2.5). The increase is most likely due to the somewhat broader molecular weight distributions that PDMB and, hence, PP have. The suggestion has been made that the molecular weight distribution of PDMB is broadened by a slow termination reaction during the polymerization.[8] Such a termination could be caused by impurities that are hard to remove from the monomer.

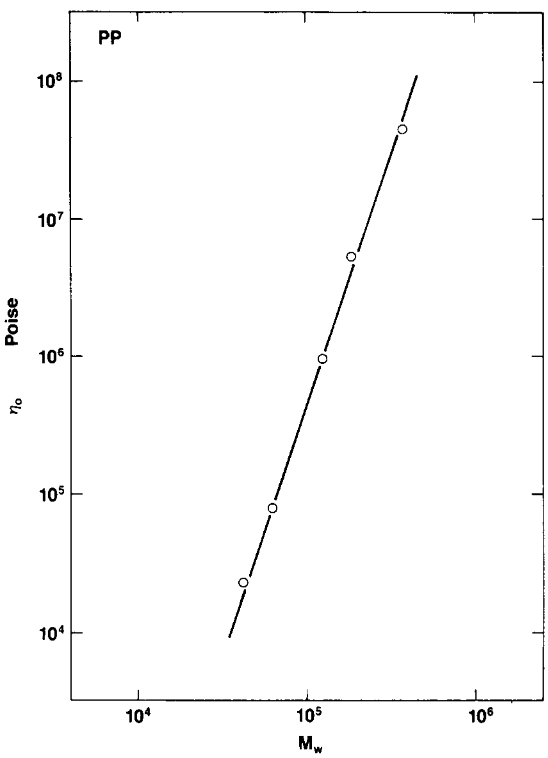

Figure 9. Molecular weight dependence of viscosity of atactic PP at 75 °C.

Molecular Weight Dependence of Viscosity. It is well established that when the molecular weight of a polymer exceeds a certain critical value, M_c, the dependence of the zero shear rate viscosity on molecular weight becomes much stronger. For $M < M_c$, $\eta_0 \propto M^{\beta'}$ where β' is approximately 1.[28] For $M > M_c$, $\eta_0 \propto M^{\beta}$ where β is typically 3.3–3.6. Because M_c is usually 2–3 times M_e, all of the polymers used in this study fall in the latter region. In Figure 9 the viscosity of the polypropylene polymers at 75 °C is shown as a function of weight average molecular weight. The data are well described by the following equation.

$$\eta_0 = 5.3_4 \times 10^{-13} M_w^{3.5_9} \text{ P} \qquad \text{(PP)} \qquad (13)$$

As indicated in the Introduction, commercial polypropylene is isotactic and has a crystalline melting point near 170 °C. Because of this, rheological studies are typically carried out in the temperature range 190–250 °C. In order to compare the present results with these data, we have corrected all available viscosities to 190 °C. For our polymers and the polymer studied by Plazek,[16] we did this with the WLF equation using parameters listed above. For the other materials where measurements were made much closer to 190 °C, we used an activation energy of 10 kcal. Three of the studies[3,6,7] did not report absolute values of M_w but did give intrinsic viscosities in tetralin at 135 °C. We estimated M_w in these cases with Parrini's equation for isotactic polypropylene.[13]

Figure 10 shows the viscosity of polypropylene as a function of M_w at 190 °C. The solid line represents the relationship between the two obtained in this study. The experimental data from the other sources[3,4,6,7,16] are somewhat scattered but on average are very close to our results. We conclude that the viscosity of PP does not depend on whether the polymer is isotactic or atactic.

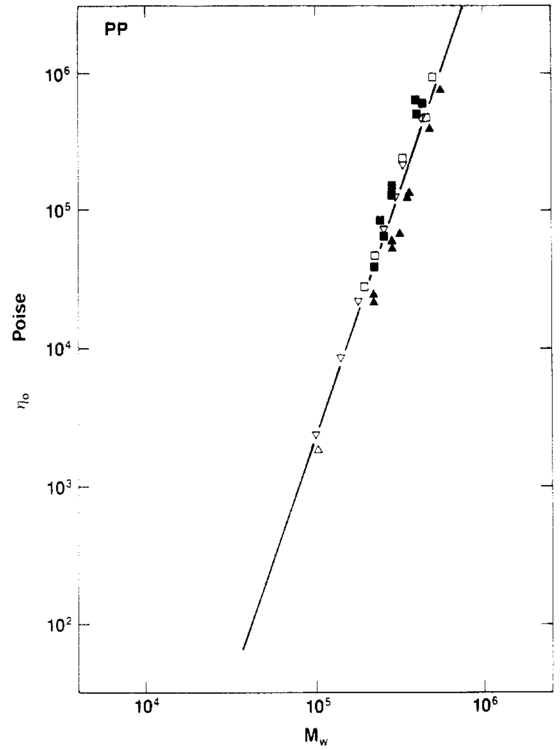

Figure 10. Molecular weight dependence of viscosity of isotactic PP at 190 °C: (□) ref 2; (▲) ref 3; (■) ref 5; (▽) ref 6; (△) ref 14; solid line, this work.

Therefore, the materials synthesized here are good model polymers for studying the rheologial behavior of polypropylene in the liquid state.

The viscosity of PDMB is shown in Figure 11 as a function of M_w at 75 °C. The data are well described by

$$\eta_0 = 1.0_4 \times 10^{-12} M_w^{3.5_6}\ \mathrm{P} \qquad \text{(PDMB)} \qquad (14)$$

To our knowledge, no other data on the viscosity–molecular weight relationship of PDMB have been reported.

It is of interest to determine whether the ratio of the viscosity of these two polymers is consistent with current molecular theory. According to the reptation model η of an entangled polymer can be related to experimental observations by[29]

$$\eta \propto \rho f(M/M_e)\tau_A \qquad (15)$$

where ρ is the density and τ_A is the relaxation time of a section of a polymer chain between entanglement points. In the original version of the reptation theory the function f is proportional to M^3:

$$f(M/M_e) \propto (M/M_e)^3 \qquad (16)$$

By studying the effect of fluctuations in the length of the "primitive path," Doi(30) was able to show that over a wide range of molecular weights f(M/M$_e$) is better approximated by a stronger power law:

$$f(M/M_e) \propto (M/M_e)^{3.5} \qquad (17)$$

Choosing the latter form for f, the viscosity ratio of two polymers with the same M but different values of ρ, M_e, and τ_A would be

$$\frac{\eta_1}{\eta_2} = \left[\frac{\rho_1}{\rho_2}\right]\left[\frac{M_{e2}}{M_{e1}}\right]^{3.5}\left[\frac{\tau_{A1}}{\tau_{A2}}\right] \qquad (18)$$

The time constant τ_A can be estimated by methods given in Ferry's book,[31] but we choose instead a similar procedure recently described by Osaki.[32] In this method the time constant τ_A is determined by matching the dynamic moduli

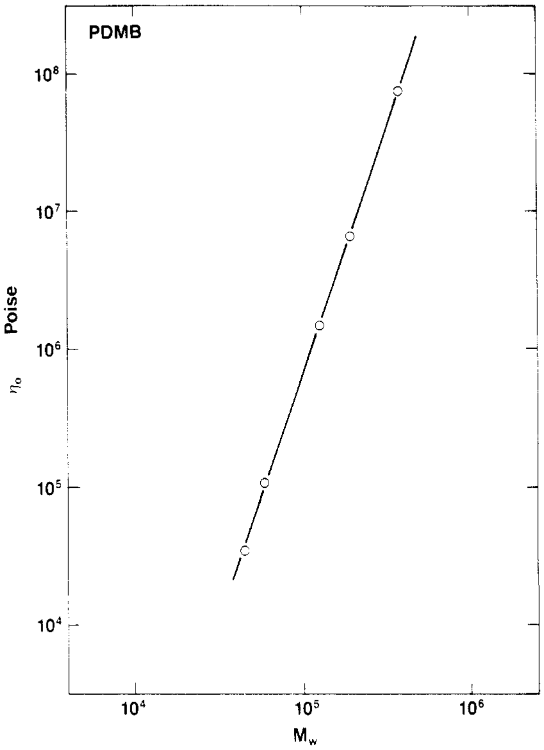

Figure 11. Molecular weight dependence of viscosity of PDMB at 75 °C.

of a Rouse chain of molecular weight M_e to the experimental values of $G'(\omega)$ and $G''(\omega)$ in the transition region. (A more complete description is given in the Appendix.) Using this technique, we find that at 75 °C the two time constants are about an order of magnitude different.

$$\tau_A = 1.9_3 \times 10^{-6}\ \mathrm{s} \qquad \text{(PP)} \qquad (19)$$

$$\tau_A = 1.9_6 \times 10^{-5}\ \mathrm{s} \qquad \text{(PDMB)} \qquad (20)$$

Substituting these values in eq 16, we find that the ratio of viscosities, $\eta(\mathrm{PP})/\eta(\mathrm{PDMB})$, is 0.30. This is in fair agreement with the average value of $\eta(\mathrm{PP})/\eta(\mathrm{PDMB})$ = 0.70 derived from the data given in Table II.

The time constants τ_A can also be used to determine the friction coefficient, ζ_0, per monomer. According to the Rouse model the longest relaxation time for a chain between entanglements is

$$\tau_A = \frac{M_e^2}{M_0}\,\frac{[\langle R^2\rangle/M]}{6\pi kT}\zeta_0 \qquad (21)$$

where $\langle R^2\rangle/M$ is a constant relating the mean square end-to-end distance of a chain to its molecular weight and M_0 is the molecular weight per monomer. Values of $\langle R^2\rangle$/M for these two polymers have been reported.[8,33]

In order that the comparison of the frictional resistance for PP and PDMB be for the same fractional length of chain, we choose for both polymers a repeat unit containing four backbone carbon atoms. The friction per propylene monomer is one half of this value. With these definitions we find that at 75 °C ζ_0 equals 2.84×10^{-7} and 1.55×10^{-6} (dyn·s)/cm for PP and PDMB, respectively. At T_g + 100 °C the two friction factors are 6.8×10^{-8} and 2.06×10^{-7} for PP and PDMB, respectively. These latter values are approximately the same as those reported by Ferry[31] for similar olefinic polymers or unsaturated rubbers.

Conclusions

Linear viscoelastic properties were determined for a series of atactic polypropylenes that were prepared in a previous study[8] by saturating poly(1,3-dimethyl-1-butenylene) with a Pd on $CaCO_3$ catalyst. The experiments covered a wide range of molecular weights and were useful for establishing the molecular weight dependence of viscosity as well as the molecular weight between entanglements and the monomeric friction factor. When the results are compared with data on commercial isotactic polypropylene, it is found that the viscosity of the two types of polymer has essentially the same molecular weight and temperature dependence. Hence polymers prepared in the manner described in this report proved to be useful model materials for studying the rheological properties of polypropylene in the liquid state. The anionic polymerization method used in their synthesis produces polymers with narrow molecular weight distributions and, in principle, can also be used to make branched polymers and block copolymers of propylene with other monomers.

A parallel study was conducted to determine the linear viscoelastic properties of the unsaturated precursor polymer poly(1,3-dimethyl-1-butenylene). It was shown that the viscosity before and after saturation is consistent with changes in the monomeric friction factor and the expected[21] changes that were found in the molecular weight between entanglements. Additional studies in which the rheological properties of anionically polymerized polymers were determined before and after saturation can be found in ref 25, 26, and 34.

Appendix

Doi's model[35] for the linear viscoelastic response of an entangled polymer shows the same characteristic features as the data presented in this paper. His prediction for the stress relaxation modulus is given by

$$G(t) = G_N \mu_C(t) \mu_A(t) \qquad \text{(A1)}$$

where $\mu_C(t)$ represents the terminal relaxation process of a chain disentangling from its neighbors and $\mu_A(t)$ describes the fast relaxation process of the sections of the chain between entanglement constraints. The function $\mu_C(t)$ is expected to relax on a time scale τ_C proportional to M^3 or somewhat higher power of M if other relaxation processes are included.[25] The function $\mu_A(t)$ describes the dynamics of a chain fixed at each end by entanglements. It is expected to have Rouse-like[35] relaxation times $\tau_A \propto M_e^2$

$$\mu_A(t) = 1 + \sum_{p=1}^{N_e} \exp(-tp^2/\tau_A) \qquad \text{(A2a)}$$

$$\tau_A = \frac{\zeta_0 b^2 N_e^2}{6\pi^2 kT} \qquad \text{(A2b)}$$

where b is a monomer length[36] and N_e is the number of monomers between entanglements. If $\tau_C \gg \tau_A$, then at times $t < \tau_A$ eq A1 will reduce to

$$G(t) = G_N + G_N \mu_R(t) \qquad \text{(A3)}$$

where $\mu_R(t) = \mu_A(t) - 1$. The function $\mu_R(t)$ is the normalized Rouse relaxation function for a free chain of length N_e. By taking the Fourier transform of eq A3, the dynamic moduli appropriate at high frequencies ($\omega > \tau_A^{-1}$) are obtained:

$$G'(\omega) = G_N + G_N \mu_R'(\omega) \qquad \text{(A4a)}$$

$$G''(\omega) = G_N \mu_R''(\omega) \qquad \text{(A4b)}$$

The procedure used in the analysis consisted of constructing the function in eq A4b from the known value of G_N and the values of $\mu_R''(\omega\tau_A)$ tabulated in Ferry's book.[37] The value of τ_A is then determined from the shift along the frequency axis required to superimpose eq A4b onto the experimental values of $G''(\omega)$. Further details can be obtained in the paper by Osaki, Nishimura, and Kurata.[32]

Registry No. PP, 9003-07-0; (*E*)-$H_2C{=}C(CH_3)CH{=}CHCH_3$, 26714-20-5.

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Fetters, L. J., unpublished results). Thus, the parameter $\langle R^2\rangle/M$ was corrected to 75 °C and T_g + 100 °C. A similar change in $\langle R^2\rangle/M$ for the two above temperatures was not done for PDMB since both theory and experiment indicate that d ln $\langle R^2\rangle/\mathrm{d}T$ for sterreoirregular polydienes is ca. 0, e.g., see: Mays, J. W.; Hadjichristidis, N.; Graessley, W. W.; Fetters, L. J. *J. Polym. Sci., Polym. Phys. Ed.* **1986**, *24*, 2553 and references contained therein.

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On the Electrostatic Contribution to the Persistence Length of Flexible Polyelectrolytes

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ABSTRACT: Quasi-elastic light scattering methods were used to study the dynamics of dilute solutions of high molecular weight ($M_p = 10^7$ daltons) poly(acrylate) for $[\mathrm{KCl}]_{\mathrm{added}}$ = 0.00, 0.05, and 0.10 M. The correlation functions were analyzed by a third-order cumulant and an overlay histogram with exponential sampling methods of analysis. The histograms exhibited a bimodal distribution. It is argued that the fast mode evident in the histograms is associated with the pure translational diffusion process for PAA-K and that the slow mode may be associated with hindered diffusion through cages formed by neighboring polyions. The ionic strength dependence of the translational diffusion coefficient is interpreted in terms of a *minor increase* in both the excluded-volume parameter and the persistence length, where these parameters eventually reach a limiting value as the ionic strength is lowered. The failure of the current theoretical models of the electrostatic component to adequately describe this ionic strength dependence of the persistence length is discussed in detail.

Introduction

The physical characteristics of polymer solutions are intimately associated with the flexibility of the polymer. The shear rate dependence of the viscosity, for example, is strongly affected by the flexibility characteristics of the polymer, where the more rigid and elongated polymers have the greater tendency to align with the hydrodynamic flow field. Variation of the solvent character greatly alters the statistical characteristics of the polymer. The effect of the solvent character is quantitatively defined, for example, by the scaling law parameter ν, viz., $R_G \propto M_p^{\nu}$. A polymer in a good solvent is highly extended because of pairwise intrasegmental repulsion which leads to the Flory limit $\nu = 0.60$. A similar situation occurs in aqueous polyelectrolyte solution where the ionic strength is varied. Intuitively one would expect the polyelectrolyte to be highly extended in the limit of zero added salt due to the repulsion between the neighboring charged groups.

Interest in the persistence length of polyelectrolytes was stimulated by the studies of Manning counterion condensation onto the surface of rodlike polyions.[1-5] The interaction potential between the ith and jth groups on the same chain was assumed to be a screened Coulomb pairwise interaction, viz.,

$$V_{i,j} = (q_{\mathrm{net}}/\epsilon)(|i-j|b)^{-1}\exp(-|i-j|b/\lambda_{\mathrm{DH}}) \tag{1}$$

where q_{net} is the net charge on the group, ϵ is the bulk dielectric constant, b is the average spacing between neighboring charges, and λ_{DH} is the Debye–Hückel screening length,

$$\lambda_{\mathrm{DH}} = (1000/8\pi N_A \lambda_B I)^{1/2} \tag{2}$$

where λ_B is the Bjerrum length,

$$\lambda_B = e^2/\epsilon kT \tag{3}$$

kT is the thermal energy, N_A is Avogadro's number, e is the magnitude of the elecron charge, ϵ is the bulk dielectric constant, and I is the ionic strength of the solution,

$$I = (1/2)\sum_j Z_j^2 C_j \tag{4}$$

where Z_j is the magnitude of the charge of the jth species of concentration C_j. A major conclusion drawn from the Manning theory in the linearized Poisson–Boltzmann limit is that counterions will condense onto the linear structure if $b < \lambda_B$; i.e., the maximum linear charge density that can be supported by the solvent is given by the Bjerrum length. The "transition" at which counterion condensation will occur is when the Manning parameter $\xi_M = \lambda_B/b$ becomes unity. A similar conclusion was made by Russel[6] for the nonlinearized Poisson–Boltzmann expression.

Skolnick and Fixman[7] and Odijk[8] independently examined the electrostatic component to the persistence length by using a mean-field approximation in the limit of the rigid-rod configuration. The major assumption in these models was that the polyelectrolyte undergoes minor deviations from the rodlike configuration such that one can express the elastic constant for bending, γ, as the sum of two terms, an intrinsic part γ_0 and an electrostatic part γ_{el}, as given by Yamakawa,[9] viz.,

$$\gamma = \gamma_0 + \gamma_{\mathrm{el}} \tag{5}$$

It is further assumed that γ_{el} is independent of the radius of curvature. Hence the potential of energy of bending is given by

$$\langle V\rangle = \left\langle (1/2)\gamma_0\int_0^L (\partial^2 r/\partial s^2)^2\,\mathrm{d}s\right\rangle + \left\langle (1/2)\gamma_{\mathrm{el}}\int_0^L (\partial^2 r/\partial s^2)^2\,\mathrm{d}s\right\rangle \tag{6}$$

Upon defining the persistence length by the wormlike coil model as $L_p = \gamma kT$, it follows from eq 5 that

$$L_p = L_0 + L_{\mathrm{el}} \tag{7}$$

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