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Influence of Syndiotactic Propylene Units on the Rheological Parameters of Poly(ethylene−propylene) Copolymers

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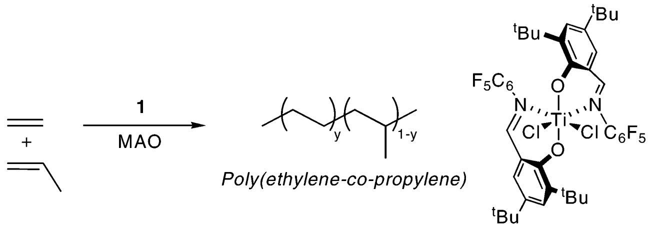
ABSTRACT: The plateau modulus has been measured for a trio of amorphous poly(ethylene−propylene) copolymers where the mole fraction of ethylene ranged from 0.57 to 0.67. These materials were prepared by using a living catalyst system involving bis(salicylaldiminato)titanium activated by methylaluminoxane. This catalyst with propylene yields highly syndiotactic (*rr* = 0.98; *rrrr* = 0.96) homopolymer. *s*-Polypropylene is known to have a plateau modulus and unperturbed chain dimension that are markedly larger than the values shared by the *atactic* and *isotactic* counterparts. The enhancement in the unperturbed chain dimension translates into an entanglement molecular weight for *s*-polypropylene that is ~1/3 that of the *atactic* and *isotactic* counterparts. Thus, within the confines of the packing length notion, these empirical observations raise the question as to whether the rheological characteristics of the *s*-polypropylene will carry over into the random copolymer format. The copolymers with *s*-polypropylene segments yield (at 348 K) larger entanglement densities (~0.39/nm^3) than the corresponding conventional materials (~0.23/nm^3). These findings demonstrate that ethylene/propylene copolymers can be prepared so as to provide a high-performance elastomeric amorphous polyolefin with a low glass transition temperature (~215 K).

Introduction

The preparation[1] of highly syndiotactic polypropylene (*s*-PP) allows us to test the hypothesis that there could be a range of propylene contents for poly(ethylene−propylene) copolymers that would have an entanglement density above those of the conventional commercial ethylene−propylene materials where the propylene segments enter in either the *atactic* or *isotactic* formats. This anticipated behavior is based upon the observed *s*-PP unperturbed chain dimension[2] and plateau modulus[3] relative to the smaller values[3−5] exhibited by the *atactic* and *isotactic* analogues. These new ethylene−propylene copolymers (prepared via a living olefin polymerization)[1] may be of practical interest since such elastomers would hold more fillers and oil extenders than the current commercial products while mimicking the latter's tensile performance. The copolymer preparative protocol involves bis(salicylaldiminato)titanium (**1**) activated by methylaluminoxane (MAO) as the living catalyst system.[1]

Experimental Section

Copolymer Synthesis. The ethylene/propylene copolymers P(E/*s*P) were prepared[1] in toluene at 0 °C. Compositions were selected so that the resulting materials would be amorphous (containing neither ethylene- nor propylene-based crystallinity). All air- and moisture-sensitive chemistry was carried out in a Braun Labmaster drybox or using standard Schlenk line techniques. The solvents were dried on solvent columns containing molecular sieves, alumina and activated copper.



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Propylene (Matheson, Polymer Grade) was purified by a column of molecular sieves and alumina. Ethylene (Matheson, Polymer Grade) was used as received.

Sample 1-6a. A 6 oz. Lab-Crest glass pressure reaction vessel (Andrews Glass) was charged with MAO (0.30 g, [Al]/[Ti] = 250) and toluene (50 mL). The reactor was placed in an ice bath. The nitrogen atmosphere in the reactor was exchanged with propylene three times. Propylene was condensed into the reactor for 30 min at 30 psi. The ethylene was reacted at 31 psi. The catalyst solution (19 mg in 5 mL toluene) was injected by syringe. After 90 min, acidic methanol (1 mL) was added by syringe to quench the polymerization. The reactor was vented and the polymer precipitated in acidic methanol (400 mL). After stirring for several hours, the polymer was filtered, washed with methanol, and dried (2.27 g, M_n = 482 kg/mol; M_w/M_n = 1.18).

Sample 2-227a. A 6 oz. Lab-Crest glass pressure reaction vessel was charged with MAO (0.30 g, [Al]/[Ti] = 500) and toluene (100 mL). The reactor was placed in an ice bath. The nitrogen atmosphere in the reactor was exchanged with propylene three times. Propylene was condensed into the reactor for 30 min at 30 psi. Ethylene was added at 40 psi. The catalyst solution (9 mg in 5 mL toluene) was injected by syringe. After 60 min, acidic methanol (1 mL) was added by syringe to quench the polymerization. The reactor was vented and the polymer precipitated in acidic methanol (400 mL). After stirring for several hours, the polymer was filtered, washed with methanol, and dried (3.05 g, M_n = 528 kg/mol; M_w/M_n = 1.18).

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Table 1. Molecular Characteristics of P(E/*s*P) Copolymers

sample	m_b (g/mol)	T_g (K)	M_n (kg/mol)	M_w (kg/mol)
1-6a	17.0	215	482	569
2-227a	16.6	214	528	641
2-12	16.4	214	537	680

Table 2. ^{13}C NMR Sequence Distribution Data for P(E/*s*P) Copolymers

sample	xn,1	xn,2	xn,3	xn,4	xn,5	xn,6
1-6a	0.279	0.244	0.162	0.095	0.075	0.145
2-227a	0.235	0.232	0.166	0.098	0.054	0.215
2-12	0.181	0.210	0.145	0.101	0.073	0.291

Sample 2-12. A 6 oz. Lab-Crest glass pressure reaction vessel (Andrews Glass) was charged with MAO (0.19 g, [Al]/[Ti] = 300) and toluene (100 mL). The reactor was placed in an ice bath. The nitrogen atmosphere in the reactor was exchanged with propylene three times. Propylene was condensed into the reactor for 30 min at 20 psi. The ethylene tank was attached at 20 psi. The catalyst solution (19 mg in 5 mL of toluene) was injected by syringe. After 60 min, acidic methanol was added by syringe to quench the polymerization. The reactor was vented and the polymer precipitated in acidic methanol. After stirring for 1 h, the polymer was filtered, washed with methanol, and dried (1.8 g, M_n = 537 kg/mol; M_w/M_n = 1.27).

Polymer Characterization. The 125 MHz ^{13}C NMR data were acquired on a Varian Inova 500 spectrometer. The polymer samples were placed in a 5 mm NMR tube with 1,1,2,2-tetrachloroethane-d_2 and dissolved by heating. The NMR spectra were referenced to nondeuterated solvent shifts at 130 °C, and data were acquired using a 5 s relaxation delay. Quantitative structural information was obtained and calculated according to published procedures.[7]

The molecular weights (M_n and M_w) and polydispersity indices (M_w/M_n) were measured by a Waters Alliance GPCV 2000 size exclusion chromatograph (SEC). The SEC columns (four Waters HT 6E and one Waters HT 2) used as the eluent 1,2,4-trichlorobenzene containing 0.01 wt % di-*tert*-butylhydroxytoluene (BHT) at 1.0 mL/min at 140 °C. The molecular weights (M_n and M_w) and polydispersity indices (M_w/M_n) were measured relative to a polyethylene calibration curve. DSC analysis was performed on a TA Instruments Q1000 equipped with a liquid nitrogen cooling system and automated sampler. Typical DSC experiments were made in crimped aluminum pans under nitrogen with a heating rate of 10 °C/min from −50 to +200 °C. The reported DSC data from the second heating run were processed with the TA Q Series software. Table 1 contains these characterization results. Table 2 contains the sequence distribution data from the ^{13}C NMR.

Rheology. Three P(E/*s*P) copolymers (Table 1) were used in this study. These P(E/*s*P) samples are compared to random PEP's[8−13] and the nearly alternating PEP[4,8,9] derived from the hydrogenation of butyllithium prepared polyisoprene. For the purposes of sample identification the acronyms P(E/*s*P) will be used for the samples prepared and evaluated in this work (Tables 1 and 2), while PEP will be used to identify the poly(ethylene−propylene) samples described in Table 3.

Rheological evaluation of the P(E/*s*P) samples was carried out using a Rheometrics Scientific ARES rheometer equipped with 8 and 10 mm parallel plate fixtures. RSI Ochestrator software was used to automatically derive master curves at a reference temperature (T_0) of 348 K by a two-dimensional minimization technique. Figures 1−3 display the storage moduli, $G'(\omega)$, the loss moduli, $G''(\omega)$, the loss tangent, tan δ, and the dynamic viscosity, η'. Note that the latter parameter reaches the Newtonian regime for all three samples. This was not possible for T_0 = 298 K. Literature data for polyethylene[14−16] (PE) and polypropylene[2−4,17,18] (PP) are also provided in Table 3.

Different data treatment methods were used to evaluate the plateau moduli of the P(E/*s*P) samples. Inspection of Figures 1−3 reveals an extended data set for G' where the gradient is virtually zero. This occurs over the (ω) range of ~10^0 to ~10^6 s^{-1}. Hence, the direct evaluation of G_N^0 from the storage modulus plot is feasible. This measurement is aided by the large entanglement density of our samples (see below). However, researchers often have difficulty in obtaining such clear indications of the plateau for other polymers due to limitations of molecular weight or accessible temperatures. This has given rise to many methods for estimating G_N^0 from limited data sets. Here we have five of those methods, outlined below, so that the reader can make an easier connection of the values given here to those of other polymers. They are as follows:

(i) Integration of the $G''(\omega)$ Disperson.[19] This involves the integration of the loss moduli G'' in the terminal zone and yields

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

where the units are in MPa. The data were treated following the procedure of Colby.[20] The terminal loss modulus was separated from the transition response by fitting $G''(\omega)$ to a

Table 3. Rheological and Molecular Parameters for PEP, P(E/*s*P), PE, and PP

sample	MFE[a]	G_N^0 (MPa)	M_e (g/mol)	$\langle R^2\rangle_0/M$ (Å^2 mol/g)	p (Å)	T_0 (K)
			PEP			
alt-PEP [8,9]	0.50	1.15	1850	0.946	2.05	298
JDF [10]	0.56	1.26	1690			298
BGRS-2 [11]	0.56	1.20	1780			300
JBG-11[8,12,13]	0.60	1.58	1350			298
BGRS-1 [11]	0.65	1.20	1780			300
			(PE/*s*P)			
1-6a	0.57	2.10	1140			348
2-227a	0.63	1.71	1450			348
2-12	0.67	1.85	1340			348
			PE			
PE [14]	1	3.50[b]	600	1.40	1.39	298
PE [15,16]	1	2.60	1040	1.25	1.69	413
			PP			
a-PP[4,17,18]	0	0.47	4500	0.677	2.88	298
a-PP	0			0.674	2.99	348
a-PP[4]	0	0.47	5800	0.669	3.14	413
a-PP[3]	0	0.43	6880	0.656	3.30	463
i-PP [3]	0	0.42	7040	0.649	3.28	463
s-PP[2,3]	0	1.35	2260	1.03	2.10	463

[a] Mole fraction of ethylene. [b] Amorphous fraction of polyethylene. See ref 4.

Table 4. Measured Plateau Moduli and Viscosities for P(E/*s*P) Copolymer (T_0 = 348 K)

	analytical method (MPa)							
sample	$3.56[G'']_{(\max)}$	crossover	tan δ	via G'' plateau	G integral	van Gurp	mean value	η_0 (MPa s)
1-6a	1.87	1.74	2.20	2.20	2.35	2.21	2.10 ± 0.24	5.77
2-227a	1.65	1.67	1.73	1.73	1.76	1.74	1.71 ± 0.043	9.73
2-12	1.76	2.04	1.82	1.82	1.83		1.85 ± 0.11	22.7

power law.[20] These data are shown in Figures 4−6 in terms of $G''(\omega)$. The dashed line is the high-frequency extrapolation of the loss modulus.

(ii) tan δ Minimum.[3] This method of estimating G_N^0 is to equate it to the value of the storage modulus, $G'(\omega)$, where tan δ is at its minimum in the plateau zone.

$$G_N^0 = (G')_{\tan\delta \to \min} \tag{2}$$

(iii) Crossover Modulus Method.[21] This procedure was developed by Wu[21] and relies on the observation that the crossover parameters in the terminal zone are correlated to the sample molecular weight distribution in terms of M_w/M_n.

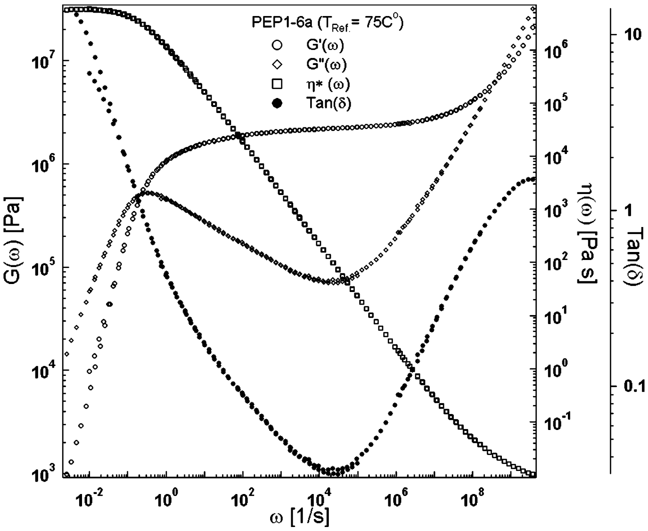


Figure 1. Master curve of the storage modulus, $G'(\omega)$, the loss modulus, $G''(\omega)$, and dynamic viscosity η^* of P(E/*s*P) 1-6a vs angular frequency (ω).

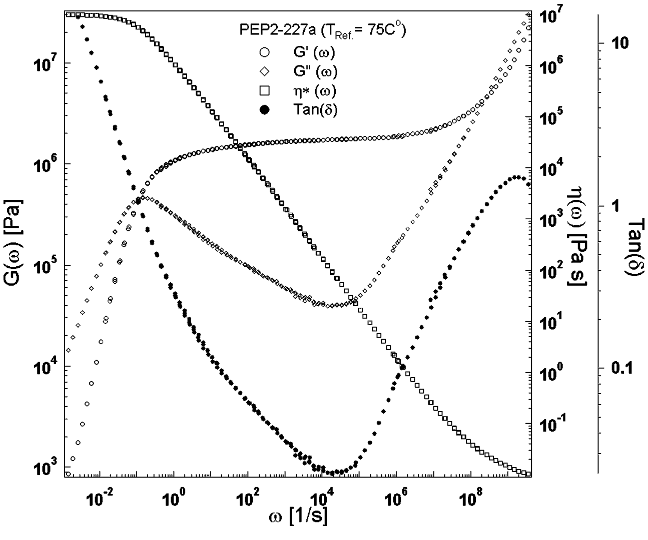


Figure 2. Master curve of the storage modulus, $G'(\omega)$, the loss modulus, $G''(\omega)$, and dynamic viscosity η^* of P(E/*s*P) 2-27a vs angular frequency (ω).

Wu's relation, which is limited for $M_w/M_n \leq 3$, follows with G_{cop} denoting the crossover modulus of the copolymer.

$$\log(G_N^0/G_{cop}) = 0.38 + [2.63 \log(M_w/M_n)/1 + 2.45(M_w/M_n)] \tag{3}$$

(iv) Empirical Method of Raju−Rachapudy−Graessley.[22] This empirical approach relates the plateau modulus to the storage modulus via a constant and $G''_{(\max)}$. This relation is valid for materials having near monodisperse molecular weight distributions.

$$G_N^0 = 3.54 G''_{(\max)} \tag{4}$$

(v) van Gurp-Palmen analyses.[23] This method plots the phase angle (δ) against the absolute value of the complex modulus ($|G^*(\omega)|$. The specimen phase angle can be identified with the ratio of its viscous and elastic components as its behavior follows the absolute value of the complex modulus. The minimum in the plot defines the plateau modulus.

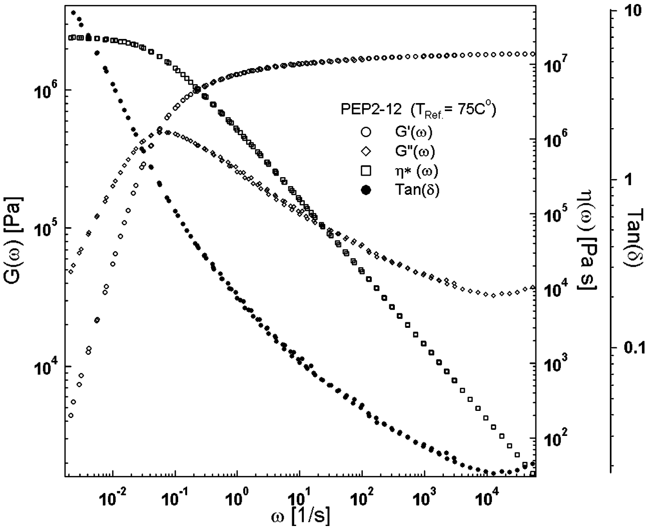


Figure 3. Master curve of the storage modulus, $G'(\omega)$, the loss modulus, $G''(\omega)$, and dynamic viscosity η^* of P(E/*s*P) 2-12 vs angular frequency (ω).

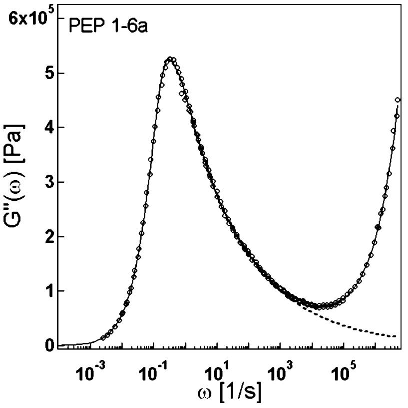


Figure 4. Loss moduli, $G''(\omega)$, for P(E/*s*P) 1-6a vs angular frequency (ω).

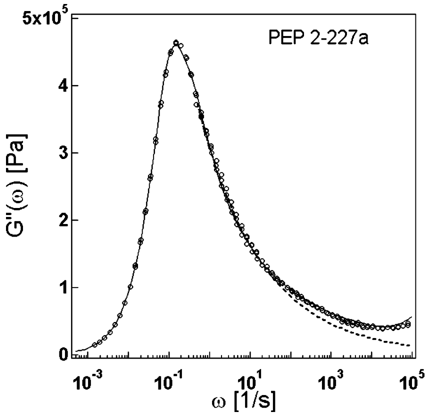


Figure 5. Loss moduli, $G''(\omega)$, for P(E/*s*P) 2-27a vs angular frequency (ω).

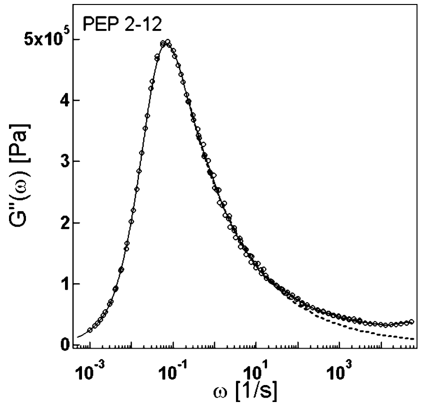


Figure 6. Loss moduli, $G''(\omega)$, for P(E/sP) 2-12 vs angular frequency (ω).

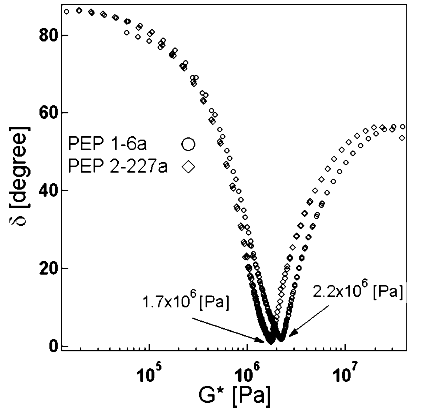


Figure 7. Van Gurp−Palmen plots for P(E/*s*P) 1-6a and 2-227a copolymers.

The P(E/*s*P) plateau moduli values are collated in Table 4 where it is seen that the agreement in the measured G_N^0 values from the different techniques is satisfactory. Figures 1−3 give G', G'', tan δ, and the dynamic viscosity, η'. Figures 4−6 show the G'' data (in the linear scale) while Figure 7 is the van Gurp−Palmen presentation. The entanglement molecular weights (M_e) are based upon the G_N^0 values of Table 4. The plateau modulus is connected to the entanglement molecular weight (M_e) by[19]

$$M_e = \frac{\rho RT}{G_N^0} \tag{5}$$

where ρ denotes the polyolefin density (0.824 g/cm^3 at 348 K and 0.855 g/cm^3 at 298 K), R the gas constant (8.314 J mol^{-1} K^{-1}), and T the absolute temperature. In eq 5 we have chosen a front factor of 1 rather than $^4/_5$, which is also often used to define M_e. We chose this to be most consistent with common usage; see our previous papers for the reasons for doing so.[24,25]

The unperturbed chain dimensions are directly relatable to the plateau modulus from the following empirical relation:[24,25]

$$\langle R^2\rangle/M_0 = P_e^{2/3}[G_N^0/kT]^{1/3}[\rho N_{av}]^{-1} \tag{6}$$

M denotes the chain molecular weight and $\langle R^2\rangle_0$ the unperturbed mean-square end-to-end distance of a chain while P_e denotes the number (20.8) of entanglement strands in a cube having the dimensions of the tube diameter,[26] k is Boltzmann's constant, and N_{av} is the Avogadro number. The P(E/*s*P) $\langle R^2\rangle_0/M$ values, derived from eq 6, along with p and m_b are listed in Table 5. The measured plateau modulus of *s*-PP (Table 3) yields, via eq 6, the unperturbed chain dimension 0.98 Å^2 mol/g. That value is in good agreement with 1.03 Å^2 mol/g determined directly from SANS measurements in the melt.[3]

Packing Length. Our rheological predictions are based upon the packing length concept[4,5,24,25] with p defined as follows in eq 7. Since $\langle R^2\rangle_0$ is proportional to molecular weight, the packing length is molecular weight independent and thus dependent only upon the local chemical structure of the polymer. The packing length is determined by comparing the volume occupied by a chain to the smallest volume that can contain the coil. Essentially, the smaller p is, the “thinner” the chain and the smaller the entanglement molecular weight.

$$p = \frac{M}{\rho N_{av}\langle R^2\rangle_0}\ (\text{Å}) \tag{7}$$

The effective chain diameter (d) is expressed[24,27] as

$$d = [4m_b/\pi l_0 \rho N_{av}]^{0.5}\ (\text{Å}) \tag{8}$$

where l_0 is the bond length, m_b is the average molecular weight per backbone bond, and V_b is the volume of that bond ($m_b/\rho N_{av}$). The packing length is alternatively given[24,27] in terms of d^2 and b_k.

$$p = \pi d^2/4b_k\ (\text{Å}) \tag{9}$$

where b_k is the Kuhn step length given by l_0C_∞ and C_∞ the Flory characteristic ratio. Thus, the packing length is directly relatable to chain “thickness”.

The following expressions[4,5] display the relations between the packing length, the plateau modulus, and entanglement molecular weight:

$$G_N^0 = \frac{kT}{P_e^2 p^3} = \frac{kT}{V_e}\ (\text{MPa}) \tag{10}$$

$$M_e = P_e^2 p^3 \rho N_{av}\ (\text{g/mol}) \tag{11}$$

$$V_e = P_e^2 p^3\ (\text{Å}^3) \tag{12}$$

Here, V_e denotes the entanglement volume. This parameter yields directly the entanglement density: $\rho_e = G_N^0/kT = 1/V_e$.

Lodge and McLeish (L−M) defined a local composition parameter,[28] ϕ_s, from the volume occupied by a Kuhn length's worth of monomers divided by V_k where $V_k \approx b_k^3$ and V_b is the volume per backbone bond. Thus, we have

$$\phi_s = [m_b C_\infty/\rho N_{av} V_k] = [l_0 p^2/V_b] \tag{13}$$

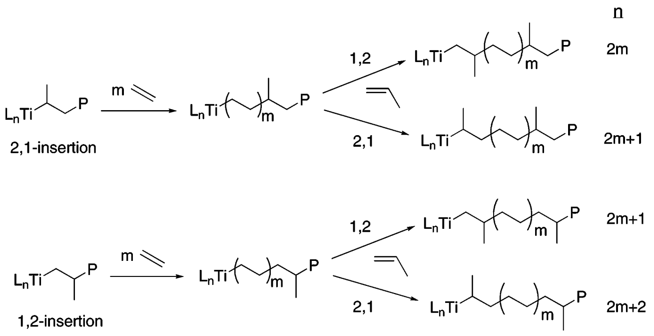
The L−M parameter is definable as the “self-concentration” of the polymer chain in the melt. Hence, ϕ_s is the volume fraction contribution of the surrounding monomer units from the same chain to the local composition. The smaller ϕ_s is, the

Table 5. Experimental P(E/*s*P) and Adjusted PEP Parameters (T_0 = 348 K)

sample	m_b (g/mol)	WFP[a]	$\langle R^2\rangle_0/M$ (Å^2 mol/g)	p (Å)	G_N^0 (MPa)	M_e[b] (g/mol)	ϕ_s	C_∞	$\kappa \times 10^3$ (K^{-1})
				P(E/*s*P)					
1-6a	17.0	0.53_1	1.15[c]	1.74	2.10	1140	0.13	8.4	
2-227a	16.6	0.46_8	1.08[c]	1.87	1.71	1400	0.14	7.7	
2-12	16.4	0.42_5	1.10[c]	1.82	1.85	1290	0.15	7.7	
				Homopolyolefins					
a-PP	21	1	0.674	2.99	0.42[d]	5700	0.33	6.0	−0.1
PE	14	0	1.33	1.51	3.20[d]	750	0.12	8.0	−1.2
				PEP					
alt-PEP	17.5	0.60_0	0.891	2.26	0.96[d]	2480	0.22	6.7	−1.2
JDF	17.1	0.54_1	0.922[e]	2.19	1.06[d]	2250	0.21	6.7	
BGRS-2	17.1	0.54_1	0.922[e]	2.19	1.06[d]	2250	0.21	6.7	
JBG-11	16.8	0.50_0	0.948[e]	2.13	1.16[d]	2060	0.21	6.8	
BGRS-1	16.5	0.44_7	0.982[e]	2.05	1.29[d]	1850	0.22	6.9	

[a] Weight fraction of polypropylene. [b] The entanglement molecular weights were derived from eq 5. [c] Via eq 6. [d] Via the use of p and eq 10. [e] Via eq 15.

Scheme 1



larger the extent of interchain contacts experienced by a single chain. Thus, M_e (and hence V_e) will decrease as ϕ_s decreases.

Results and Discussion

Polymer Structures. The bis(salicylaldiminato)-titanium/MAO catalyst system results[1] in the 2,1-insertion of propylene to produce *s*-polypropylene ([*rr*] = 0.99 and [*rrrr*] = 0.96). The homopolymerization of propylene is dominated[29] by regioregular 2,1-insertions into a secondary titanium−alkyl species. When ethylene is added as a comonomer to the polymerization of propylene, regioirregular insertions of propylene become possible (Table 2).[29] For example, after insertion of m ethylene units to give a primary titanium−alkyl species, the next propylene monomer can undergo a 2,1- or 1,2-insertion (see Scheme 1). As a result, a distribution of odd and even uninterrupted methylene sequences (n) between methine carbons is observed. The schematic reaction sequence above represents possible sequence distributions for poly(ethylene-*co*-propylene) copolymers and the resulting number of uninterrupted methylene sequences. The fraction of six or more uninterrupted methylene units (n = 6) increases with increasing ethylene content as shown in Table 2. Conversely, the isolated methylene fraction (n = 1), from adjacent propylene units, increases with increasing propylene content. The presence of these abnormal structures would be expected to lead to the subtraction of the syndiotactic chain characteristics in the copolymer. The presence of 1,2 and 2,1 propylene insertions in these copolymers makes it difficult to directly calculate the distribution of propylene or ethylene sequences, but we can say that the data in Table 2 are consistent with a random copolymerization mechanism. This means that the average length of the propylene sequences is fairly short, probably between 2.0 and 2.5 propylene repeat units. In any event, the effects of sequence distribution on plateau modulus are not well-known. The only case for which there are data are ethylene−butene copolymers of 50 mol % butene, where the alternating and random copolymers[4] have quite similar values of G_N^0.

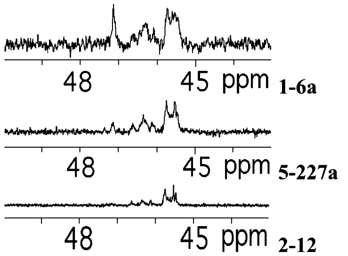


Figure 8. ^{13}C NMR signals for syndiotactic polypropylene in the P(E/*s*P) copolymers.

PEP and PE/*s*P Comparison. The packing model permits[4,5] access to the plateau modulus and the entanglement molecular weight. With the appropriate chain dimensions in place eqs 10 and 11 provide access to the basic rheological parameters for polyolefin homo- and copolymers. This is due to the following interdependencies that emerge from eqs 7−12:

$$(\langle R^2\rangle_0/M)^3 \propto G_N^0 \propto 1/M_e \tag{14}$$

The role of density can be discounted for polyolefins since that parameter is, at a given temperature, virtually identical for all amorphous poly(α-olefins), polyisobutylene being the primary exception. The various tactic forms of polypropylene show a large range of values in $\langle R^2\rangle_0/M$ with *s*-PP showing the largest size chains at a given molecular weight. For *s*-PP (Table 3) the enhancement of $\langle R^2\rangle_0/M$ is caused by the increased population of the *trans* conformers (relative to *a*-PP and *i*-PP). Rotational isomeric state calculations[30] support this trend. Within experimental error *a*-PP and *i*-PP share the same unperturbed chain dimension[18] and plateau modulus.[3]

A route to the calculation of the plateau modulus is outlined as follows. Direct knowledge of the chain dimension allows the calculation of the packing length (eq 7). A necessary complement to $\langle R^2\rangle_0/M$ is its temperature coefficient which is defined as d $\ln\langle R^2\rangle_0/\mathrm{d}T = \kappa$ (K^{-1}). For polyolefins the sign can be positive, negative, or null. With this parameter in hand the measured chain dimension can be used to calculate the appropriate packing length values at various temperatures. The values of κ for *alt*-poly(ethylene−propylene),[9] polyeth-

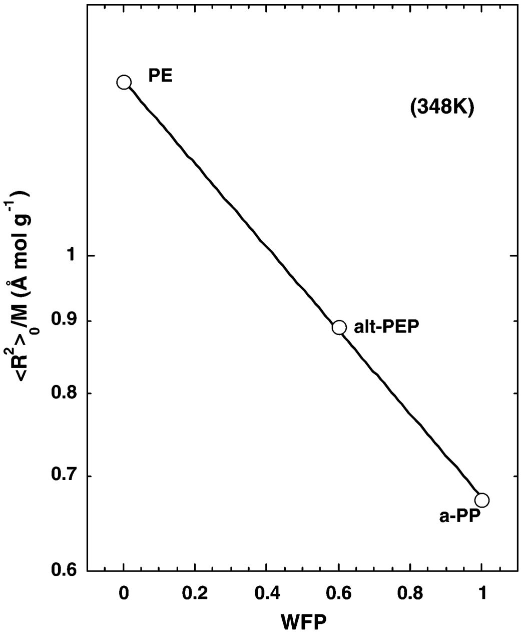


Figure 9. Semilog plot of unperturbed chain dimensions of PE, *alt*-PEP, and *a*-PP as a function of the weight fraction of propylene. The 348 K data were calculated from the measured values of κ and the chain dimensions in the melt from small-angle neutron scattering.[9,16,18]

ylene,[16] and *a*-polypropylene[18] are given in Table 5. G_N^0 for PE and PEP is strongly temperature dependent.[4] This can easily be understood in terms of the packing length model, since as temperature increases, both density and chain dimensions decrease. Use of the available *alt*-PEP, PE, and *a*-PP chain dimension (boldfaced type in Table 5) and *k* data[9,16,18] yields the packing length and thus the G_N^0 values, eq 6, for 348 K. The following expression (see Figure 9) provides the route to M_e for the PEP series via the use of eqs 5, 7, and 10.

$$\langle R^2\rangle_0/M = 1.328\mathrm{e}^{-0.67479x} \qquad (15)$$

The parameter *x* denotes the weight fraction of propylene in the PEP copolymer series. The decrease in the plateau moduli with increasing temperature mimics the previously observed[8] behavior of *alt*-PEP. The PEP and the P(E/*s*P) data are collated in Table 5.

The M_e data show that the copolymers prepared with the syndiotactic-specific catalyst exhibit enhanced (approximately 2-fold) G_N^0 values relative to their PEP counterparts. This can be seen directly in terms of the entanglement molecular weights in Table 5. The PEP family shows elevated values of M_e relative to those of P(E/*s*P). This increase in entanglement density is caused by the presence of the syndiotactic sequences in the (PE/*s*P) copolymers. The same trend is observed when the L−M parameters are cross-compared (see Table 5).

Conclusions

Random copolymers of ethylene−propylene were prepared using a catalyst with a penchant for syndiotactic placement of the propylene units. According to the packing length model, the presence of the syndiotactic structure should lead to an increase in the plateau moduli relative to that found when the propylene units are present in either the *atactic* or *isotactic* formats. The observed increase in plateau moduli is the result of the larger unperturbed chain dimension of *s*-PP, compared to *i*-PP and *a*-PP, and its subsequent influence on the P(E/*s*P) entanglement molecular weights.

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