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Notes

Effect of Tacticity on the Dilute Solution Coil Dimensions of Poly(α-olefin)s

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Introduction

Tacticity is a powerful variable in polymer material science that affects both melt and solid-state properties.[1−8] One such property is molecular coil dimensions. The impact of tacticity on molecular coil size has been studied for polypropylene,[1−3] poly(methyl methacrylate),[4−6] and polystyrene.[5,7] However, to our knowledge there have been no such studies for other poly(α-olefin)s.

In view of this knowledge gap, we undertook an investigation of tacticity's effect on the coil dimensions of polypropylene, poly(1-butene), poly(1-pentene), poly(1-hexene), and poly(1-octene). Isotactic and syndiotactic pairs of each polymer were synthesized and characterized by carbon 13 nuclear magnetic resonance (^{13}C NMR) to confirm the tacticity. Size exclusion chromatography (SEC) combined with on-line light scattering and viscometer detectors was used to measure dilute solution coil dimensions of the samples.[9] Two SEC configurations were used in this work: one with on-line refractive index and multiangle light scattering detection (SEC-MALLS) and the other with refractive index, low-angle light scattering, and viscometric detection (SEC-LALLS-VIS). The narrow distribution fractions emerging from the SEC columns were directed through detectors whose outputs were used to determine concentration *c*, molecular weight MW, radius of gyration R_g (SEC-MALLS only), and intrinsic viscosity $[\eta]$ (SEC-LALLS-VIS only) on a continuous basis. The solvent used in all cases was 1,2,4-trichlorobenzene (TCB) at 135 °C, which is a good solvent for the polymers studied here.

Experimental Section

Sample Preparation and Characterization. The syndiotactic polymers were made with isopropyl(cyclopentadienyl-1-fluorenyl)zirconiumdimethyl, **1** (MW = 518.79), activated with dimethylanilinium perfluorotetraphenylborate (DMAHD4, MW = 801.23). The isotactic polypropylene sample is an EMCC commercial sample made from a Ziegler−Natta catalyst. The remaining isotactic polymers were made either with *rac*-(dimethylsilyl)bis(2-methyl-4-phenylindenyl)zirconiumdimethyl, **2** (MW = 587.98), or with *rac*-(dimethylsilyl)bis(indenyl)hafniumdimethyl), **3** (MW = 495.01), activated with DMAHD4. Polymerizations with condensable monomers were carried out using monomer that had been freshly purified by passing through a column of activated basic alumina inside a nitrogen-purged Vacuum Atmospheres drybox. Catalysts were prepared in dry toluene by combining a one-to-one mole ratio of metallocene and activator at ambient temperature for ∼30 min. All condensable monomer polymerizations were carried out at ambient temperature in dried glassware equipped with a magnetic stirrer inside the drybox. Butene polymerizations were carried out in a 2 L stainless steel autoclave charged with 300 mL of purified butane-1.

^{13}C NMR spectra were collected using a 500 MHz NMR made by Varian Corp.

SEC Equipment, Calibration, and Operating Procedure. The details of the SEC equipment, calibration, and operating procedure have been described previously and will not be repeated here.[9] Readers interested in knowing these details are directed to the reference indicated.

Results

Table 1 lists the molecular weights, M_w/M_n, major resonances, and % of the dominant diads of the samples studied. Figure 1 shows the ^{13}C NMR spectra obtained for the isotactic poly(1-hexene) sample. All samples exhibit >88% *m* or *r* diads in accordance with their tacticity. The average *m* or *r* diad level is 94%. The relative degree of microstructural perfection tends to decrease with increasing α-olefin length. Spectra are dominated by a few resonances, and the number corresponds to the number of unique carbons based on the dominant microstructure expected. The positions of the major resonances are also consistent with the assigned structures. Consequently, the spectra confirm that the samples have the expected tacticities.

The samples listed in Table 1 were run in triplicate (or more) on both SEC setups. The methodologies for determining the correct light scattering and viscometry coefficients for analyzing the MALLS, LALLS, and viscometry data have been described in detail previously.[9] Figure 2a,b plots R_g and $[\eta]$ as a function of molecular weight for the polypropylene and polyoctene pairs. Also plotted are the coil dimensions of a syndiotactic propylene−ethylene copolymer containing 11 wt % ethylene; the significance of this sample will be discussed later. The samples studied exhibit molecular weight scaling laws:

$$R_g = K_s M^{\alpha_s} \tag{1}$$

$$[\eta] = K_v M^{\alpha_v} \tag{2}$$

As was done previously, the data were fit to the functional forms above using coefficients of $\alpha_s = 0.580$ and $\alpha_v = 0.695$.[9] Table 1 lists the K_s and K_v obtained. Figure 3 plots g_{SCB} and g'_{SCB}. Here g_{SCB} and g'_{SCB} are defined as

$$g_{\mathrm{SCB}} = \frac{{K_s}^2}{({K_s}^2)_{\mathrm{PE}}} \tag{3}$$

$$g'_{\mathrm{SCB}} = \frac{K_v}{(K_v)_{\mathrm{PE}}} \tag{4}$$

where $(K_s)_{\mathrm{PE}}$ and $(K_v)_{\mathrm{PE}}$ are the K_s and K_v values for

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Table 1. Molecular Structure of Poly(α-olefin) Pairs[a]

polymer	M_w (g/mol)	M_w/M_n (DRI)	major resonances (ppm)	% *r* (*m*) diads	$K_s \times 10^2$ (nm)	$K_v \times 10^4$ (dL/g)
i-polypropylene	177 000	3.10	21.8, 29.0, 46.6	(98)	1.73	2.62
s-polypropylene	256 000	2.13	20.3, 28.5, 47.1	94.5[10]	1.99	3.90
i-poly(1-butene)	169 000	1.89	10.9, 27.8, 35.1, 40.3	(97)	1.52	1.81
s-poly(1-butene)	99 000	1.87	10.7, 26.9, 34.7, 40.7	94	1.74	2.76
i-poly(1-pentene)	46 000	2.08	14.6, 19.7, 33.2, 38.0, 41.1	(>97)	1.50	1.77
s-poly(1-pentene)	153 000	2.00	14.8, 19.3, 33.4, 37.5, 41.9	96	1.68	2.48
i-poly(1-hexene)	77 000	1.92	14.2, 23.4, 29.1, 33.4, 35.3, 41.2	(91)	1.44	1.54
s-poly(1-hexene)	65 000	2.24	14.1, 23.4, 29.2, 33.7, 34.6, 42.1	88	1.56	1.89
i-poly(1-octene)	154 000	3.06	14.1, 23.0, 26.9, 30.2, 32.2, 33.4, 35.6, 41.2	(93)	1.38	1.31
s-poly(1-octene)	72 000	2.20	14.1, 22.9, 26.9, 30.2, 32.2, 33.6, 34.9, 41.9	91	1.44	1.55

[a] M_w values listed are from the SEC-MALLS. The LALLS detector was calibrated such that the M_w value measured matches (on average) the value obtained from the MALLS. For the 10 samples studied we find an average discrepancy between the detectors of 0.5% with a standard deviation of 1.5%.

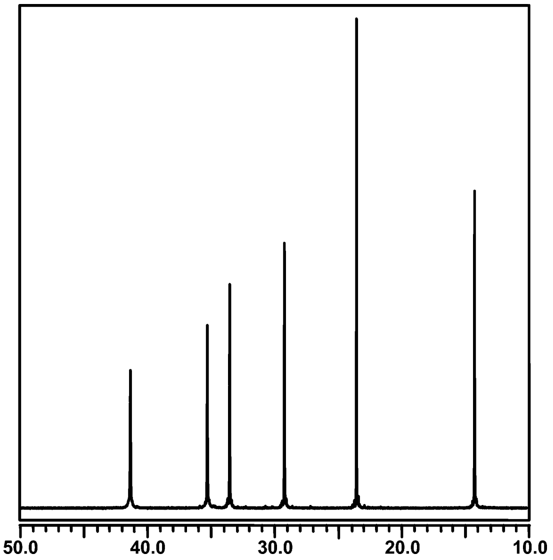

Figure 1. ^{13}C NMR spectra of isotactic poly(1-hexene) sample. Units of *x*-axis are ppm.

linear homopolyethylene in TCB at 135 °C.[9] We use previously determined values of $(K_s)_{PE} = 2.30 \times 10^{-2}$ nm and $(K_v)_{PE} = 5.79 \times 10^{-4}$ dL/g.[9]

Discussion

Both the R_g and $[\eta]$ measurements show that syndiotactic poly(α-olefins) exhibit significantly enhanced coil dimensions in dilute solution relative to their isotactic counterparts. This feature is most prominent for polypropylene, in which the syndiotactic form exhibits an R_g and $[\eta]$ that are 15% and 49% higher than the isotactic form. The difference steadily decreases with increasing α-olefin length to 4.5% and 18% for poly(1-octene). This trend suggests that factors other than tacticity, such as side-group crowding, play an increasingly greater role in determining persistence length with increasing α-olefin length.

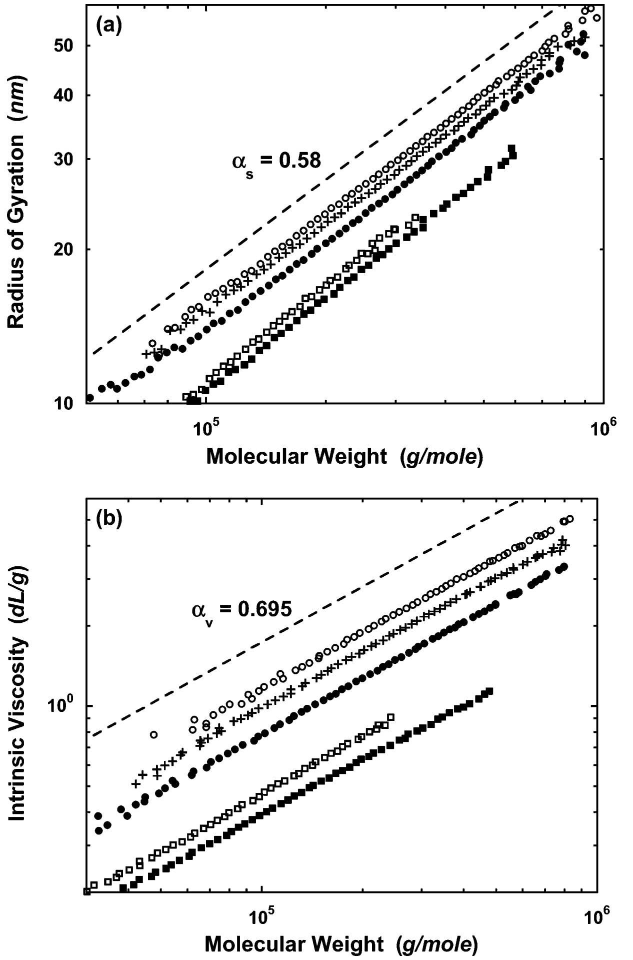

Figure 2. Coil dimension as a function of molecular weight for the polypropylene and polyoctene pairs. (a) R_g vs MW. The dashed line represents a 0.58 scaling law. (b) $[\eta]$ vs MW. The dashed line represents a 0.695 scaling law. In order of decreasing coil size are syndiotactic polypropylene (○), 89/11 syndiotactic propylene−ethylene copolymer (+), isotactic polypropylene (●), syndiotactic polyoctene (□), and isotactic polyoctene (■).

Good solvent, dilute solution coil measurements have several advantages over small-angle neutron scattering (SANS). Some examples are the ability to work with polydisperse samples (when combined with SEC), less expensive equipment, and not having to synthesize deuterated samples. However, melt coil dimensions measured by SANS using appropriately labeled and nearly monodisperse polymers are still widely accepted as the best measurements. Melt coil dimensions can be used to predict rheological properties, such as entanglement molecular weight, plateau modulus, and polymer miscibility.[11,12] For this reason it would be useful to compare the dilute solution measurements to melt SANS measurements. To our knowledge, of the polymer pairs studied here SANS measurements in the melt have only been performed on polypropylene. Jones et al. measured segment lengths of 6.2 and 7.6 Å for isotactic and syndiotactic polypropylene, respectively, which corresponds to a 23% difference in R_g.[3] Similarly, plateau moduli measurements ($\propto \langle R_g^2 \rangle_{melt}^3$) of 0.43 and

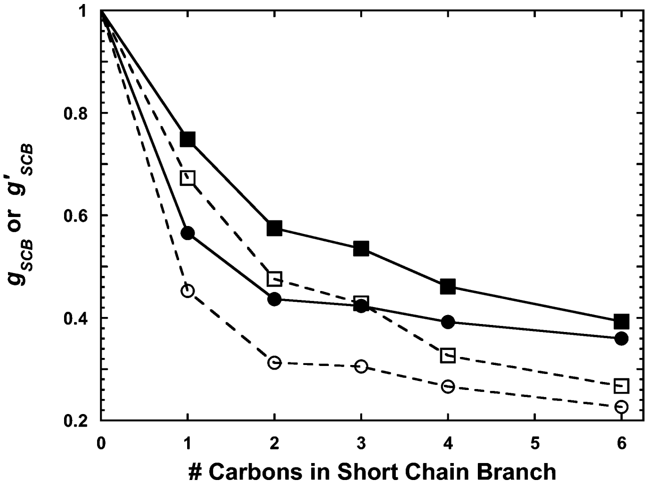

Figure 3. Plot of g_{SCB} (solid symbols) and g'_{SCB} (open symbols) for isotactic and syndiotactic poly(α-olefins). The solid symbols represent g_{SCB} for isotactic (●) and syndiotactic (■) polymers. The open symbols represent g'_{SCB} for isotactic (○) and syndiotactic (□) polymers.

1.35 MPa respectively for isotactic and syndiotactic polypropylene imply a 21% difference.[2,11] In contrast, the good solvent, dilute solution measurements reported here show a 15% difference, a discrepancy possibly due to variations in excluded-volume effects.

In Figure 2 we plotted the coil dimensions of a propylene−ethylene copolymer of 11 wt % ethylene made by the syndiotactic catalyst used to make the syndiotactic homopolymers.[13] Hereafter, we refer to this sample as s-89/11 PE. ^{13}C NMR confirmed that the sample has syndiotactic propylene placements. We now discuss the significance of s-89/11 PE. In a previous work it was found that the addition of short chain branches (SCB) causes a depression in coil dimensions for poly(α-olefin) copolymers made with isotactic catalysts.[9] It was proposed that coil dimensions for poly(α-olefin)s is determined solely by the proportion of carbon atoms in the backbone, a model referred to as the backbone model. The model exhibited significant quantitative deviations from the data. However, it seemed qualitatively correct in that it successfully predicted that coil dimensions would decrease with increasing SCB. The backbone model prediction for s-89/11 PE would be that the coil dimensions should increase relative to syndiotactic homopolypropylene because the addition of ethylene units increases the proportion of carbon atoms in the backbone. However, in contrast to what was found for isotactic copolymers, the addition of ethylene *depressed* the coil size. The implication is that the backbone model fails not just quantitatively, but qualitatively, in predicting the coil dimensions of syndiotactic copolymers. It is speculated that the addition of ethylene creates degrees of freedom in the syndiotactic polypropylene coil that depress coil dimensions.

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