On the Structure of Syndiotactic Poly(propylenes)

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ABSTRACT

Propylene was polymerized with the catalyst system $(C_2H_5)_2AlCl/$ $VCl_4/$ anisole at $-78°C$ using various conditions. The resulting polymers were successively extracted by diethyl ether, hexane, and heptane, leaving the residue. The polymers of the four series were characterized by intrinsic viscosity, gel permeation chromatography, ^{13}C nuclear magnetic resonance, infrared spectroscopy, x-ray diffraction, and by differential scanning calorimetry. The combined evidence from the various methods indicates that this catalyst system leads to stereoblock polymers which can be fractionated according to stereochemical composition and sequence length.

INTRODUCTION

The chemical structure and the physical properties of predominantly syndiotactic poly(propylenes) (st-PP) have been studied by many research groups since the first representative of this class of polymers was synthesized by Natta et al. [1]. Later studies by the Natta group [2, 3] revealed that the highest syndiotacticities result from the catalyst system $VCl_4/(C_2H_5)_2AlCl/anisole$ (see also Refs. 4

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and 5). Whether the highest syndiotacticity observed is also the highest syndiotacticity possible has long been a matter of discussion. Earlier claims that the reported st-PP had a low content of isotactic diads [6], were even free of detectable isotactic and heterotactic triads [7], or had at least a uniform distribution of syndiotactic units [8] could not be confirmed by later research (see below). Rather the existence of long syndiotactic stereoblocks was suspected, based on the existence of two melting temperatures [9], studies of the polymerization mechanism [10], and the infrared spectra of crystalline polymers [6]. The presence of blends of isotactic and syndiotactic polymer molecules can, of course, not be ruled out either [9]. Depending on polymerization conditions, the polymers may furthermore contain nonnegligible amounts of head-to-head and tail-to-tail connections [4, 5, 11, 12].

The constitutional and configurational differences among the various "syndiotactic" poly(propylenes) undoubtedly affect their properties, especially their solution properties. We have been interested in this problem since we could show that the tendency of poly(propylene) toward association in solution depends on the tacticity and that association becomes significant if the mole fraction of syndiotactic diads exceeds 70-80% [4, 9]. We also suspected an effect of configurational sequence length on the association behavior [9] as was later demonstrated for poly(methyl methacrylates) of various tacticities [13]. Such association studies obviously require well-characterized samples. We have thus studied the configurational composition of syndiotactic poly(propylenes) and their fractions, using the catalyst system VCl_4/$(C_2H_5)_2AlCl$ with or without anisole.

EXPERIMENTAL

Polymerizations

Propylene was polymerized by the modified Natta method [3, 4, 6, 7, 10] using a 1-L neck flask as reactor. The flask was partially filled with solvent (see Table 1) and cooled to -78°C. The catalyst components were added in a nitrogen atmosphere under stirring and the polymerization was started by adding gaseous or liquid propylene, keeping a constant polymerization temperature of -78°C. The polymerization was terminated by adding an excess amount of methanol containing some hydrochloric acid. The precipitated polymer was washed several times with methanol, dissolved in cyclohexane, precipitated with methanol, and dried in a vacuum oven. The white color of the polymers indicated the absence of catalyst residues (VCl_4: brown; VCl_2: green).

TABLE 1. Polymerization Conditions

	Polymerization no.						
	1	2	3	4	5	6	7
Catalyst:							
$(C_2H_5)_2AlCl$ (mmol)	29.0	41.4	78.6	39.3	41.4	20.7	41.4
VCl_4 (mmol)	4.0	4.7	9.9	4.7	4.7	4.7	9.4
Anisole (mmol)	0	4.0	0	4.6	4.6	4.6	9.2
t-Butylperbenzoate (mL)	0	0	0.43	0	0	0	0
Reaction conditions:							
Toluene[a] (mL)	400	0	0	0	0	0	0
Hexanes[a] (mL)	0	350	350	0	0	0	0
Heptane[b] (mL)	0	0	0	350	350	350	350
Propylene (mL)	400[c]	400[c]	400[c]	400[c]	400[c]	354[d]	270[d]
Reaction time (h)	22	19	18	20	5.0	6.0	6.0
Polymer yield (g)	17.0	4.9	7.0	12.2	17.4	5.0	12.8

[a] Aldrich Chemical grade.
[b] Distilled after treating the solvent with Na metal for a week.
[c] Introduced as gas.
[d] Liquid propylene.

Fractionations

Polymerization products were extracted under reflux with an insulated extractor for 24 h each, first with diethyl ether (E), then with hexane (HX) (mixture of isomers), and finally with heptane (HP). An exception is Polymer 6 which was first extracted with heptane and then with hexanes. The resulting solutions were each concentrated with a rotary evaporator and then poured into methanol. The precipitated polymer was dried as described above.

Viscosities and Molar Masses

Intrinsic viscosities $[\eta]$ were determined in heptane at $30°C$ using an Ubbelohde-type viscometer. Viscosity-average molar masses were calculated via [14]

$$[\eta] = 0.0312M_V^{0.71} \text{ mL/g} \tag{1}$$

Ratios of weight-average to number-average molar masses (M_w/M_n) were obtained from measurements of 1% polymer solutions in chloroform using a Perkin-Elmer Liquid Chromatograph, Model 601, equipped with micro-styragel columns with pore diameters of 10^3 and 10^4 Å. The columns were calibrated with poly(styrene) standards (see also Ref. 15).

Differential Scanning Calorimetry (DSC)

Melting temperatures and heats of fusion were determined with 5-10 mg samples at a heating rate of 40 K/min using a Perkin-Elmer Model DSC-1B. Melting temperatures were calibrated and corrected with an indium standard (melting temperature at peak position = 429.8 K). Heats of fusion were measured by the area of the fusion peak and calibrated for a known mass of indium (heat of fusion = 6.80 cal/g = 28.45 J/g).

Carbon-13 Nuclear Magnetic Resonance

Carbon-13 NMR spectra were obtained from 15% polymer solutions in 1,2,4-trichlorobenzene at $140°C$ using a JEOL JNM PS-100 spectrometer equipped with a PFT-100 Fourier transform system operating at 25.41 MHz. 2000 times of transient were accumulated at a repetition rate of 4.0 s. Hexamethyldisiloxane was used as standard. Configurational triads were assigned for the methyl carbons following the suggestion of Zambelli et al. [16]; triad contents were determined

from the areas under the peaks. The mole fractions of configura-
tional diads were calculated from the mole fractions of configura-
tional triads via

$$x_i = x_{ii} + (1/2)x_{is}$$ (2)

$$x_s = x_{ss} + (1/2)x_{is}$$ (3)

where x_{ii}, x_{ss}, and x_{is} are the mole fractions of isotactic (ii), syndio-
tactic (ss), and heterotactic triads (is), respectively. Number-average
sequence lengths (in propylene units) of configurational homosequences
were calculated from Ref. 17:

$$\overline{n}_i = 2x_i/x_{is}$$ (4)

$$\overline{n}_s = 2x_s/x_{is}$$ (5)

Infrared (IR) Spectroscopy

Polymers were pressed into films which were annealed 1 h at 90°C
(fractions designated E) or 120°C (all others). Spectra were recorded
with a Beckman Model IR 20A-X infrared spectrometer with a scan-
ning speed of 240 cm^{-1}/min. The intensity of the peak at 868 cm^{-1},
generally assigned to syndiotactic sequences [18], did not change
much by annealing.

X-Ray Diffraction

X-ray spectra were measured at films, using a Philips X-ray
diffractometer Model SRG-3000 with wide angle goniometer and nickel-
filtered CuK radiation (λ = 0.1542 nm).

RESULTS

Configuration

Polymer 1 was totally soluble in diethyl ether whereas all the other
polymers contained various amounts of polymer insoluble in this
solvent (Table 2). Addition of anisole to the catalyst resulted in
increasing amounts of material insoluble in diethyl ether (Polymers

TABLE 2. Yields of Polymer Fractions after Extraction with Diethyl Ether (E), Hexane (HX), or Heptane (HP). R = Residue

Polymer no.	Fraction in wt%			
	E	HX	HP	R
1	100	No experiment		0
5	85	No experiment		15
3	82	No experiment		18
2	72	No experiment		28
4	60	24	4	12
7	50	34	9	7
6	26	51	19	4

2-7) which increased with decreasing ratio Al/V [cf. Polymers 6 and 7 with $(C_2H_5)_2AlCl/VCl_4$ = 4.4 mmol/mmol vs Polymers 2-5 with 7.9-8.9 mmol/mmol]. No attempt was made, however, to clarify the relationships between catalyst composition and reaction conditions on one hand and polymer solubility and composition on the other because our primary objective was the preparation of polymers with various configurational compositions and not a mechanistic study.

The diethyl ether soluble fractions of Polymers 1-5 showed molar masses and molar mass ratios similar to those obtained by Doi et al. [19] (Table 3). All polymers of this E series exhibited bimodal molar mass distribution curves, the only exception being Polymer 1 (1-E) with a unimodal distribution curve (Fig. 1). This polymer is also the only one which is totally soluble in diethyl ether.

The diethyl ether fractions are predominantly syndiotactic according to NMR spectra (Fig. 2, Table 4). Their syndiotactic triad content varies between 0.49 and 0.60, depending slightly on polymerization conditions. Remarkable is the practically constant fraction of heterotactic triads (x_{is} = 0.29 ± 0.016). The triad heterotacticity is thus almost twice as high as that for the hexane/heptane soluble fractions (x_{is} = 0.16 ± 0.016) which is also independent of the polymerization conditions. The syndiotactic triad content of the HX/HP fractions, on the other hand, is in the same range as the syndiotactic triad content of the E series (0.44-0.73 vs 0.49-0.60). As a result, both the average isotactic and the average syndiotactic sequence lengths are higher for HX/HP fractions than for E fractions.

The configurational statistics of both the E and the HX/HP series does not follow Bernoulli statistics since the heterotacticity index HI = $x_{is}/(x_{ii}x_{ss})^{1/2}$ is always smaller than 2 (Table 5). If one assumes a

TABLE 3. Measured Intrinsic Viscosities, $[\eta]$, Calculated Viscosity-Average Molar Masses, M_v, and Molar Mass Ratios, M_w/M_n, of Some Diethyl Ether Soluble Fractions

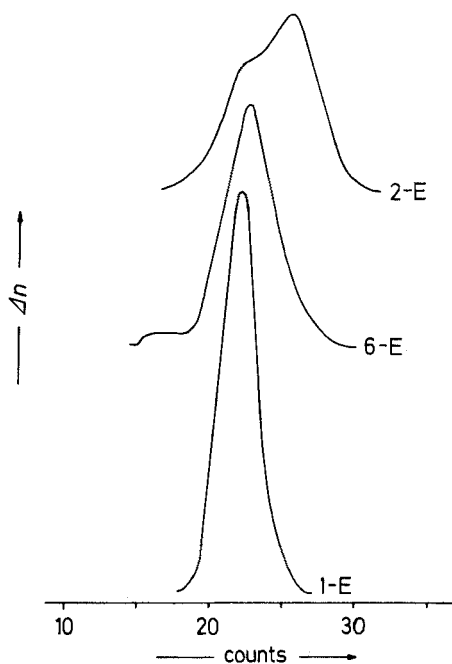| Polymer no.	$\dfrac{[\eta]}{(mL/g^{-1})}$	$\dfrac{10^{-3}\ M_v}{(g/mol^{-1})}$	M_w/M_n
1-E	47.5	30.4	1.54
5-E	–	–	3.00
3-E	30.5	16.3	6.19
2-E	23.0	10.9	3.61
4-E	–	–	4.83

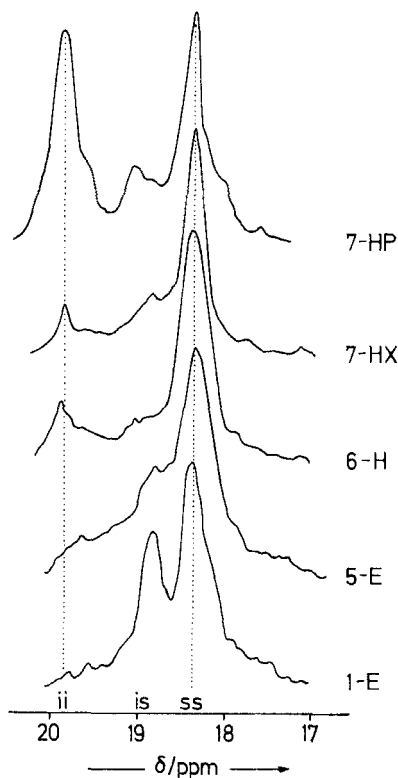FIG. 1. Gel permeation chromatograms of diethyl ether soluble fractions of various polymers.

FIG. 2. Configurational triad sensitive region of ^{13}C NMR spectra of various fractions.

Markov first-order statistics, then the conditional probabilities $p_{s/s}$, $p_{s/i}$, $p_{i/s}$, and $p_{i/i}$ can be calculated from [20]

$$x_{ii} \equiv x_i p_{i/i}; \qquad p_{i/i} + p_{i/s} \equiv 1 \qquad (6)$$

$$x_{ss} \equiv x_s p_{s/s}; \qquad p_{s/s} + p_{s/i} \equiv 1 \qquad (7)$$

The conditional probabilities $p_{s/s}$ are constant for each series and, consequentely, so are the conditional probabilities $p_{s/i}$ (Table 5). The conditional probabilities $p_{i/i}$ and $p_{i/s}$ vary, however, with polymerization conditions. The relatively high values of $p_{s/s}$ for each series,

TABLE 4. Configurational Parameters of Polymers

Polymer	Triad fractions			Diad fractions		Sequence lengths	
	x_{ss}	x_{is}	x_{ii}	x_s	x_i	$\bar{n}_s$	$\bar{n}_i$
1-E	0.603	0.315	0.082	0.760	0.240	4.8	1.5
5-E	0.582	0.298	0.120	0.731	0.269	4.9	1.8
3-E	0.487	0.305	0.208	0.640	0.360	4.2	2.4
2-E	0.534	0.282	0.184	0.675	0.325	4.8	2.3
4-E	0.598	0.275	0.127	0.736	0.264	5.4	1.9
4-HX	0.730	0.161	0.109	0.810	0.199	10.1	2.5
7-HX	0.646	0.178	0.176	0.735	0.265	8.3	3.0
6-H[a]	0.640	0.145	0.215	0.712	0.288	9.8	4.0
7-HP	0.438	0.142	0.420	0.509	0.491	7.2	6.9

[a]Polymer from heptane extraction before extraction by hexanes (see text).

i.e., 0.79 (E series) and 0.89 (H series), indicate a tendency toward formation of long syndiotactic stereosequences. However, the conditional probabilities $p_{i/i}$ can reach very high values, too, especially for the heptane-soluble fractions. This behavior suggests a blockiness of the polymers. It should be emphasized, however, that the configurational statistics does not follow a simple Markov statistics as we will show elsewhere [21].

We also checked whether the data follow the enantiomorphic site model [22] as has been suggested for both the isospecific and the syndiospecific polymerizations of propylene [23]. In this model the ratio x_{ss}/x_{is} should always equal 1/2. Such a value is neither found for the E fractions nor for the H fractions (Table 5). Since the relations between various triad types must be independent of the type of fraction [24], i.e., E or H fractions, the enantiomorphic site model cannot apply to these syndiospecific polymerizations.

Crystallinity

Infrared spectra confirm the presence of stereoregular sequences in the H fractions (Fig. 3). The spectra show bands at 998 and 841 cm^{-1} which are thought to be due to helical isotactic poly(propylene)

TABLE 5. Heterotacticity Indices HI, Enantiomorphicity Ratio EI, and Conditional Probabilities $p_{s/s} = 1 - p_{s/i}$ and $p_{i/i} = 1 - p_{i/s}$ for Some Fractions

Fraction	$HI = x_{is}/(x_{ii}x_{ss})^{1/2}$	Conditional probabilities		$EI = x_{ss}/x_{is}$
		$p_{s/s}$	$p_{i/i}$	
1-E	1.42	0.793	0.342	1.91
5-E	1.13	0.796	0.446	1.95
3-E	0.96	0.761	0.578	1.60
2-E	0.90	0.791	0.566	1.89
4-E	1.00	0.812	0.481	2.17
Average	1.1 ± 0.21	0.79 ± 0.019	n.a.	1.9 ± 0.20
4-HX	0.57	0.901	0.548	4.53
7-HX	0.53	0.879	0.664	3.62
6-H	0.39	0.899	0.764	4.41
7-HP	0.33	0.861	0.855	3.08
Average	0.5 ± 0.11	0.89 ± 0.019	n.a.	3.9 ± 0.68

sequences with at least 10-12 propylene units per sequence [18]. The isotactic regularity band at 973 cm^{-1} overlaps with the syndiotactic helix band at 977 cm^{-1}. The syndiotactic helix band at 867 cm^{-1} is very pronounced whereas the syndiotactic regularity band at 962 cm^{-1} appears at a shoulder.

We also studied x-ray diffraction patterns since they can be used to identify the crystallized isotactic and syndiotactic portions. Syndiotactic poly(propylene) shows distinct peaks at $2\theta = 12.2$, 15.9, and 20.5° [2, 3, 8, 14] whereas isotactic poly(propylene) has very distinct peaks at $2\theta = 13.8$, 17, 18.5, and 21.2/21.7° [3].

The x-ray pattern of our Fraction 7-E is practically identical to that of a syndiotactic poly(propylene) of Zambelli et al. [3]. Syndiotactic peaks are more or less pronounced, but isotactic peaks are mainly present as shoulders only (Fig. 4). The syndiotactic peaks become more prominent in the hexane extract (Fraction 7-HX) where the isotactic peaks are very weak. The heptane Extract 7-HP, on the other hand, shows slightly reduced syndiotactic peaks as compared to 7-HX but greatly increased isotactic peaks. Finally, the Residue 7-R exhibits an x-ray pattern very similar to the one published for an authentic isotactic PP [3]: strong isotactic peaks and almost no syndiotactic peaks.
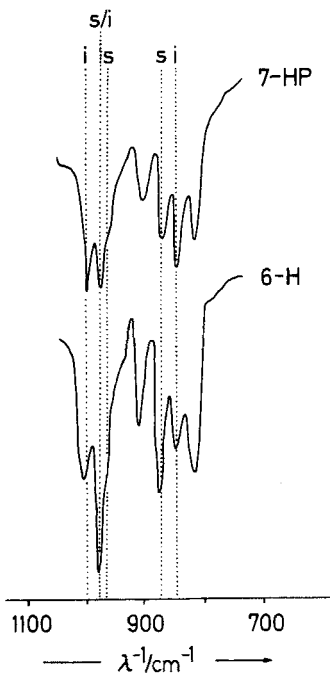
FIG. 3. Section of IR spectra of Fractions 7-HP and 6-H. Configuration sensitive bands are marked by "i" or "s."

In addition, heats of fusion were determined via DSC measurements (Fig. 5). The values obtained ranged between 530 and 1940 J/(mol unit) (Table 6) which agrees well with the literature values of 7.0 cal/g = 1234 J/(mol unit) [7]. The melting temperatures vary between 116 and 140°C (Table 6), the highest of which is higher than the "best" literature value of 131°C for syndiotactic poly(propylene) [25] but lower than the "ultimate" melting temperature of 161°C [25]. The melting temperatures increase with increasing heat of fusion. No relationship could be found between the melting temperature or the heat of fusion on one hand and the syndiotactic diad content or the average configurational sequence length on the other.

CONCLUSIONS

Poly(propylenes) obtained with the syndiospecific catalyst $(C_2H_5)_2$-AlCl/VCl /anisole are neither totally soluble in diethyl ether nor in hydrocarbons below 40°C, contrary to the statement in a previous
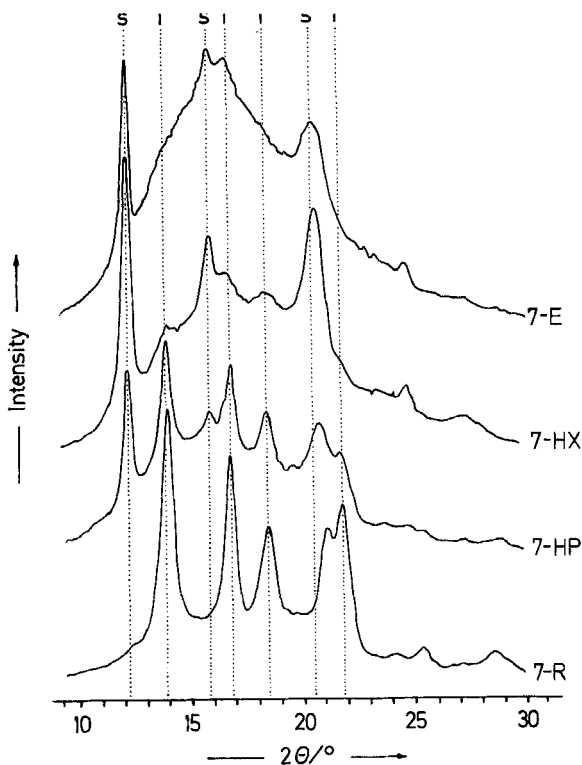
FIG. 4. X-ray diffraction patterns for the E, HX, HP, and R fractions of Polymer 7. Samples were annealed for 1 h at 120°C (HX, HP, R) and 90°C (E).

review [8]. Rather, they can be fractionated by successive extraction with diethyl ether, hexanes, and heptane. The proportion of the fractions depends on polymerization conditions and thus ranges between 26 and 100% (E), 24-50% (HX), 4-19% (HP), and 0-28% (R, residue).

E-series polymers contain 53-60% syndiotactic triads, about 30% heterotactic triads, and 8-21% isotactic triads. They give the typical "syndiotactic" x-ray pattern which includes a weak "isotactic" peak at $2\theta = 17°$. The isotactic content of these fractions cannot come from the admixture of syndiotactic and isotactic molecules since it-PP does not dissolve in diethyl ether.

The H series of polymers exhibits practically the same range of syndiotactic triads (44-73%) as the E series. The H fractions contain, however, only about one-half of the heterotactic triads of the E fractions
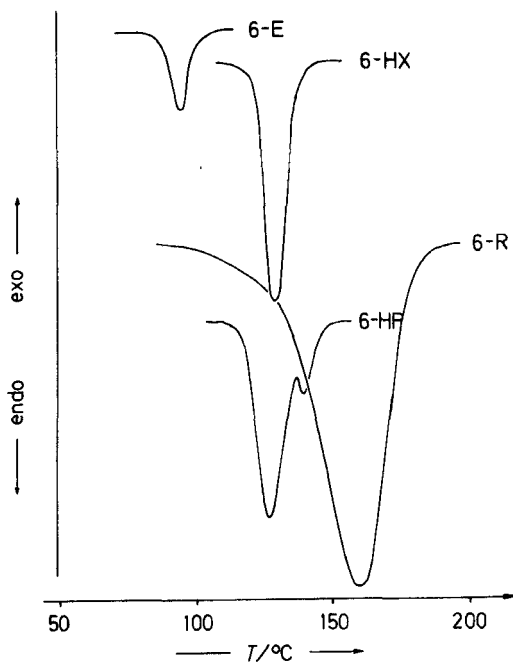
FIG. 5. DSC thermograms of the fractions of Polymer 6. The areas under the curves are proportional to the specific heat of fusion. The annealing conditions were the same as in Fig. 4.

TABLE 6. Heats of Fusion and Melting Temperatures of Polymers Annealed for 1 h at Various Temperatures

Polymer	Annealing temperature in °C	ΔH J/(mol unit)	T_M °C
7	110	–	140
6	110	1940	134
7-HX	120	1360	130
6-H	120	1250	130
4-HX	120	1085	124
4	110	529	116

which in turn doubles not only the average syndiotactic sequence length from 4-5 units to 7-10 units but also the average isotactic sequence lengths from 1.5-2.5 to 2.5-7. The heptane-soluble fraction has about the same proportion of isotactic and syndiotactic units. The residue, on the other hand, is typical isotactic.

We conclude from this combined evidence that the syndiospecific catalyst system $(C_2H_5)_2AlCl/VCl_4$/anisole leads to stereoblock polymers which can be fractionated with suitable solvents according to block length.

ACKNOWLEDGMENTS

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