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Head to Head Polymers. XVII[a]: Head to Head Polypropylene

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Head to head polypropylene was prepared by catalytic hydrogenation of either *cis*-1,4-poly(2,3-dimethylbutadiene) or *trans*-1,4-poly(2,3-dimethylbutadiene) with cobalt 2-ethylhexanoate/triethylaluminium as the hydrogenation catalyst in decahydronaphthalene solution. The hydrogenation occurred predominantly by *cis* hydrogen addition, but was not stereospecific. The samples of head to head polypropylene were characterized by IR and NMR, particularly by ^{13}C-NMR spectroscopy. The polymers were amorphous and exhibited glass transition temperatures about 20 °C lower than that of head to tail polypropylene; the glass transition temperatures were measured by DSC and varied somewhat from sample to sample (sufficiently high molecular weight) according to their stereochemistry. The T_g values were confirmed by Rheovibron measurements. The thermal stability of head to head polypropylene is not significantly different from that of either atactic or isotactic head to tail polypropylene.

[Keywords: Catalytic hydrogenation; Coordination polymerization; Glass transition temperature; 1,4-Poly(2,3-dimethylbutadiene), cis- and trans-; Polymers]

Kopf-zu-Kopf-Polymere, 17. Mitt.: Kopf-zu-Kopf-Polypropylen

Kopf-zu-Kopf-Polypropylen wurde mittels katalytischer Hydrierung von *cis*-1,4-Poly(2,3-dimethylbutadien) bzw. *trans*-1,4-Poly(2,3-dimethylbutadien) mit Kobalt-2-ethylhexanoat/Triethyl-aluminium als Katalysator dargestellt. Die Hydrierung verlief überwiegend über *cis*-Addition, war aber nicht stereospezifisch. Die Polymerproben wurden mittels IR und NMR, insbesondere ^{13}C, charakterisiert. Die erhaltenen Polymeren waren amorph und zeigten Glasübergangstemperaturen, die um etwa 20 °C niedriger waren als bei Kopf-zu-

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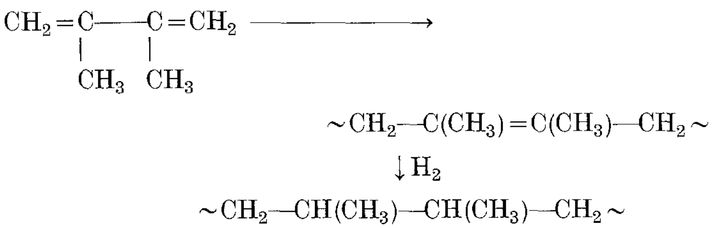
Schwanz-Polypropylen. Die thermische Stabilität von Kopf-zu-Kopf-Polypropylen ist nicht signifikant verschieden von ataktischem oder isotaktischem Kopf-zu-Schwanz-Polypropylen.

Introduction

Copolymerization of ethylene with a large excess of butene-2 in the presence of coordination initiators was carried out to obtain a 1 : 1 alternating copolymer[1] which is identical in structure to head to head polypropylene (*H-H PP*). Only after careful fractionation of the copolymer mixture was a very small amount of copolymer of unspecified molecular weight isolated which contained nearly 50% of butene-2. The polymer was analyzed by IR and X-ray diffraction, but was not characterized further.

Very recently, the synthesis of *H-H PP* by 1,4-polymerization of 2,3-dimethylbutadiene (*DMB*) followed by catalytic hydrogenation of the double bond has been reported by three groups[2–6] (Equation 1).



$$CH_2{=}\underset{CH_3}{\underset{|}{C}}-\underset{CH_3}{\underset{|}{C}}{=}CH_2 \longrightarrow$$

$$\sim CH_2-C(CH_3){=}C(CH_3)-CH_2\sim$$

$$\downarrow H_2$$

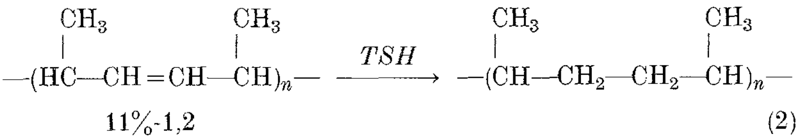
$$\sim CH_2-CH(CH_3)-CH(CH_3)-CH_2\sim \qquad (1)$$

Prudhomme[4] studied the structure of poly-*DMB* (*PDMB*) prepared by anionic initiators. High resolution ^{1}H-NMR showed that anionic polymerization of *DMB* resulted in a polymer with 74% *trans*-1,4, 23% *cis*-1,4, and 3% 1,2-structures. He also evaluated the structure of *PDMB* produced by free radical polymerization of *DMB* which led to the formation of *PDMB* with a predominance of 1,4-*trans* structures along with nearly 10% 1,2 linkages.

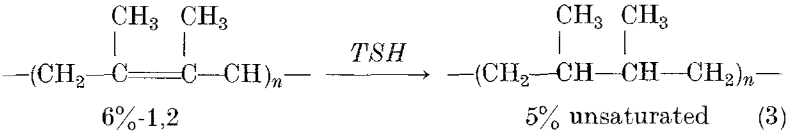
Homogeneous hydrogenation of *PDMB* was accomplished with the reaction product of triethylaluminium and the cobaltic salt of 4-cyclohexylbutanoic acid[6]. Analysis of the polymer structure by NMR techniques indicated that *cis* addition of hydrogen was favored but nevertheless non-stereospecific addition of hydrogen was proposed. Most homogeneous hydrogenations favor *cis* addition[7] but *trans* additions were observed in a few select cases involving platinum (II) and tin (III) halides.

The glass transition temperature, T_g, of the sample of *H-H PP* was measured by DSC and found to be —24 °C, which was compared to a literature value of T_g for atactic head to tail *H-T PP* of —7 °C. The value of T_g as a function of the degree of hydrogenation was also examined.

H-H PP was also obtained by the hydrogenation of two polydienes[5]: 1,4-poly(2,4-hexadiene) and 1,4-poly(2,3-dimethylbutadiene) (Equations 2 and 3).



$$\underset{11\%\text{-}1,2}{-(\overset{CH_3}{\overset{|}{HC}}-CH=CH-\overset{CH_3}{\overset{|}{CH}})_n-} \xrightarrow{TSH} -(\overset{CH_3}{\overset{|}{CH}}-CH_2-CH_2-\overset{CH_3}{\overset{|}{CH}})_n- \qquad (2)$$



$$\underset{6\%\text{-}1,2}{-(CH_2-\overset{CH_3}{\overset{|}{C}}=\overset{CH_3}{\overset{|}{C}}-CH)_n-} \xrightarrow{TSH} \underset{5\%\ \text{unsaturated}}{-(CH_2-\overset{CH_3}{\overset{|}{CH}}-\overset{CH_3}{\overset{|}{CH}}-CH_2)_n-} \qquad (3)$$

Cationic polymerization of 2,4-hexadiene produced a polymer where the proportion of 1,2-units exceeded 10%. *PDMB* was also prepared by emulsion polymerization of *DMB* and 1,2-units were found to be present at a level of at least 6%. Hydrogenation with *p*-toluene sulfonyl hydrazide (*TSH*) as the reducing agent left 5% residual unsaturation. Residual unsaturation and short chain branches present in both polymers could significantly affect many characteristic properties[8].

T_g values (by DSC) of *H-H PP* were studied as a function of their mode of preparation (Equations 2 and 3); a T_g of —17 °C was found for *H-H PP* prepared according to (Equation (2) and a T_g of —10 °C for *H-H PP* prepared by the second route (Equation 3). All values seem to be above the threshold molecular weight where T_g does not depend any more on the molecular weight. The values were compared to a literature report[9] of the T_g of atactic *H-T PP* of —6 °C. *Cowie* suggested[5], but could not confirm, that the difference of T_g's between the two samples of *H-H PP* might be due to a difference in *erythro* and *threo* configurations with longer sequences of one or the other configurations leading to various degrees of chain stiffening in the *H-H PP* samples. Mechanical damping spectra showed the T_g of *H-H PP* and *H-T* atactic *PP* to be approximately —7 °C. The unpertubed dimensions of *H-H PP* were found to be smaller than that of atactic *H-T PP*[10].

Our own earlier report[2] on the preparation of *H-H PP* involved some brief characterization; the T_g of our *H-H* sample was found to be about 20 °C lower than that of the sample of atactic *PP*. It was the objective of this work to study the hydrogenation of our carefully prepared samples of *cis*-1,4-poly(2,3-dimethylbutadiene) and *trans*-1,4-poly(2,3-dimethylbutadiene) to *H-H PP* characterize the samples, and measure selected physical and mechanical properties.

Experimental

Materials

Decahydronaphthalene (decalin), (Aldrich Chemical Co.) was heated under reflux overnight over sodium, distilled under reduced pressure (b.p. 56 °C/6 mm) and stored over sodium.

Tri-isobutylaluminium [$Al(iBu)_3$] (Ethyl Corporation) was distilled under reduced pressure (b.p. 86 °C/10 mm) and stored under nitrogen prior to use.

Cobalt-2-ethylhexanoate was used as obtained from Pfaltz and Bauer, Inc.

Cis-1,4-poly(2,3-dimethylbutadiene) (*cis-PDMB*) and *trans*-1,4-poly(2,3-dimethylbutadiene) (*trans-PDMB*) were prepared and characterized as described in our earlier paper[11].

Measurements

Infrared spectra were recorded on a Perkin-Elmer Model 727 or Model 283 spectrophotometer. Solid samples were measured as KBr pellets. The infrared spectra of some of the polymer samples were measured as films cast directly onto a single NaCl plate from an *o*-dichlorobenzene solution. The peak assignments were made to the nearest 5 cm^{-1}.

^{13}C-NMR spectra were obtained on a Varian CFT-20 spectrometer under complete proton decoupling. The measurements were carried out in *o*-dichlorobenzene at 90 °C with either an external standard of D_2O or dioxane or an internal standard of *TMS*.

Thermogravimetric analyses were performed with a Perkin-Elmer Model TGS-1 thermobalance with an UU-I temperature programmer. The temperature scale of the programmer was calibrated with the magnetic standards provided with the instrument in order to optimize the agreement between the direct dial readout of the temperature programmer and the instrument furnace temperature, as indicated by transitions of the standards. Heating rates of 20 °C/min were normally employed and all thermogravimetric measurements were performed under a 10–20 cc/min flow of dry N_2. Samples (10–20 mg) were weighed to the nearest 0.02 mg into platinum sample pans on a Perkin-Elmer AD-2 Autobalance.

Thermal transitions in the polymer samples were determined on a Perkin-Elmer Model DSC-2 differential scanning calorimeter equipped with a Scanning AutoZero unit. The temperature scale of the instrument was calibrated at the desired heating rate by adjusting the direct dial average temperature readout of the programmer to correspond with the transition temperature of cyclohexane (crystallization point —87.2 °C, melting point +6.4 °C) and indium (melting point 156.8 °C). Samples were contained in a sealed aluminium pan. Sample weights of 5–15 mg were used, and all weightings were made on a Perkin-Elmer AD-2 Autobalance.

Glass transition temperatures (T_g's) were determined from the resultant thermograms as the temperature at which the first deviation from the baseline of heat capacity (C_p) was observed. T_g values can also be reported as the temperature at which the heat capacity reaches one half of the entire step change observed.

Dynamic mechanical measurements were carried out on a Rheovibron Dynamic Viscoelastometer Model DDV II. The samples were studied in a temperature range from —140 °C to about 150 °C at a heating rate of 1-2 °C/min under dry nitrogen. The frequency of measurement was 11 Hz.

Investigations of the X-ray wide angle scattering on our samples were carried out with an X-ray beam of a wavelength of 1.5418 Å (Cu/K_α, β filtered with Ni), with the beam passing through a pinhole collimator, the samples, and finally onto a flat film camera.

Hydrogenations were carried out in 300 ml autoclave with an air driven stirrer (Parr Laboratory Reactor Co.) or in a one gallon, packed stirrer autoclave (Autoclave Engineers, Inc.).

Catalytic Homogeneous Hydrogenation of cis and trans-1,4-Poly(2,3-dimethylbutadiene)

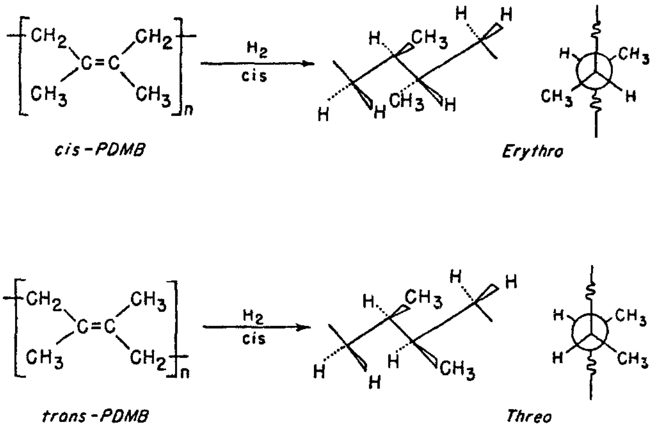
A 300 ml glass liner dried overnight at 120 °C was placed in a nitrogen filled glove bag, and allowed to cool to room temperature. In a 250 ml round bottom flask, under nitrogen, *cis-PDMB* (0.4 g, 4.8 mmol, $\eta_{\text{inh}} = 0.60$ dL/g) was dissolved in decahydronaphthalene (decalin) (80 ml) at 100 °C. The catalyst solution was prepared by allowing cobalt-2-ethylhexanoate (1.43 g, 4.1 mmol, 1.5 mmol Co) to react with $Al(iBu)_3$ (1.16 g, 5.8 mmol) in 7.5 ml of decalin. The polymer and catalyst solutions were poured into the autoclave (operation in the glove bag) and the reaction was carried out at an initial pressure of 100 p.s.i. H_2 at 100 °C for 2 h. The solution was then added dropwise to one liter of isopropanol containing 10% concentrated HCl. The precipitated polymer was filtered and gave a light-blue, tacky product. This material was dissolved in hot decalin and reprecipitated in isopropanol containing 10% concentrated HCl; this reprecipitation was done three times. The product was finally dissolved in hot decalin, reprecipitated into isopropanol, the suspension filtered, washed with 10% HCl, 10% sodium bicarbonate, water, and methanol, and then dried in an Abderhalden apparatus at 0.1 mm, 100 °C. A white tacky material (0.35 g, 88%) was obtained. The infrared spectrum (film on NaCl plate) showed absorptions from 2960 to 2850 cm^{-1} (η_{as}-CH_3, η_s-CH_2 and η_s-CH_3). Strong absorption bands were also observed at 1460 and 1380 cm^{-1} (δ_{as}-CH_3 and δ_s-CH_3). The ^{13}C-NMR spectrum showed six major peaks of chemical shifts (two for each carbon atom) at $\delta = 38.73$, 37.86 (—CH—), $\delta = 33.35$, $\delta = 31.88$ (—CH_2) and $\delta = 17.15$, 15.20 (—CH_3) (details in Table 3).

Catalytic Heterogeneous Hydrogenation of Poly(2,3-dimethylbutadiene)

Cis-1,4-*PBMD* (0.4 g, 4.9 mmol, $\eta_{\text{inh}} = 0.90$ dL/g) was dissolved in 80 ml of decalin at 100 °C. This solution was transferred to the autoclave. Pd/carbon (0.33 g) was added, the autocalve sealed, flushed with hydrogen, and pressurized to 920 p.s.i. The temperature was 130 °C (H_2 pressure rising to 1020 p.s.i.) and the hydrogenation was carried out with moderate stirring for 24 h. At the end of this period the reactor was cooled, the pressure released, and the black solution filtered through a steam-jacketed funnel containing filter paper and Celite 545 filter aid, to remove the catalyst. The Celite cake was washed with hot decalin (2 × 50 ml) to recover any polymer that might have precipitated. Decalin was removed on a rotary evaporator, and a tacky off-white polymer was recovered which had an inherent viscosity of 0.32 dL/g [0.1% in tetrahydronaphthalene (tetralin), 100 °C]. The ^{13}C-NMR spectrum showed chemical shift peaks at $\delta = 38.57$, 37.79 (—CH—), $\delta = 33.70$, 31.66 (—CH_2), $\delta = 17.26$, 15.07 (—CH_3).

Results and Discussion

Cis- and *trans-PDMB* were hydrogenated (Equation 4) with either heterogeneous or homogeneous catalyst systems and the resulting *H-H PP* was characterized.



(4)

A. Heterogeneous Hydrogenation Catalysts

Hydrogenation of unsaturated hydrocarbons with heterogeneous catalysts has been recently summarized with particular emphasis on polymer systems[12–14]. Activity for catalytic hydrogenation has been confirmed for the nine Group VIII metals[12], with nickel, palladium and platinum being the most widely investigated. *Yakubchik* and coworkers have studied the hydrogenation of polybutadiene as well as natural and synthetic polyisoprene[15–17]. Palladium and platinum have also been used successfully as catalysts for the hydrogenation of diene polymers[18, 19].

Common features required of many heterogeneous hydrogenations of polymers are high temperature, high pressure, high catalyst concentration and long reaction time. One serious problem in all polymer hydrogenations with heterogeneous catalysts has been that hydrogenation at the high temperatures and pressures employed[20] is accompanied by the serious side reaction of hydrogenolysis which results in a decrease in molecular weight.

B. Homogeneous Hydrogenation Catalysts

Homogeneous hydrogenation catalysts have distinct advantages[21] over heterogeneous hydrogenation catalysts. Reaction temperature, hydrogen pressure and catalyst concentration are low while hydrogen is taken up rapidly. Another advantage of homogeneous hydrogenation is the relative ease of workup and polymer isolation. To isolate the polymer from the catalyst, the hydrogenation solution is washed with an organic solvent containing dilute acid which destroys the catalyst.

A typical catalyst is prepared by mixing a metal alkyl (AlR_3 or $LiBu$) and an organic salt of the transition metal Ni, Co, Fe or Cr[22, 23, 7].

Table 1. *Homogeneous catalytic hydrogenation of poly(2,3-dimethylbutadiene)*[a]

	Polymer[b]			Catalysts[c]		Recovery		
Experiment	Type	η_{inh}[d] dL/g	g	$Al(iBu)_3$ in g (in mmol)	Co-II in g (in mmol Co)	g	%	η_{inh}[d] dL/g
1	*t-PDMB*	0.65	0.8	2.32 (12.0)	2.86 (3.0)	0.68	85	0.44
2	*c-PDMB*	0.90	0.8	2.32 (12.0)	2.86 (3.0)	0.75	94	0.61
3	*t-PDMB*	0.65	0.6	1.71 (8.9)	2.12 (2.2)	0.40	80	0.42
4	*c-PDMB*	0.70	1.0	2.94 (14.8)	3.59 (3.7)	0.65	65	0.51
5	*c-PDMB*	0.70	1.0	2.94 (14.8)	3.59 (3.7)	0.65	65	0.50
6[e]	*t-PDMB*	0.55	10.0	29.1 (146)	35.9 (37.0)	4.00	40	0.35

[a] Reaction temperature 100 °C; H_2 pressure = 100 p.s.i.; time = 2 h.
[b] Polymers dissolved in decalin, 0.5% solutions.
[c] A $2 \times 10^{-1} M$ solution of Co-II (cobalt-2-ethylhexanoate) in decalin.
[d] 0.1% in tetralin, 100 °C.
[e] Experiment carried out in a one gallon autoclave.

The activity of the catalyst has been shown to depend on the alkyl metal transition metal ratio, its concentration, the temperature and hydrogen pressure, as was recently shown by the versatility of the homogeneous hydrogenation of polybutadiene, polyisoprene and polystyrene[24, 25].

The selection of an appropriate hydrogenation system must be based on several factors. The most important consideration in the preparation of *H-H* polyolefins is to insure a nondestructive nature of the hydrogenation reaction along with the ease of isolation of the hydrogenated polymer. For our catalytic hydrogenation, high catalyst concentration (30 mole%) with respect to the polymer had to be employed with an Al/Co molar ratio of 4. Isolation of the hydrogenated polymer from the reaction mixture was relatively easy (Table 1).

All catalyst preparations were carried out in an inert atmosphere. When the organoaluminium compound was allowed to react with the transition metal component, the solution turned black; the reaction was allowed to continue for 10 minutes. At the end of this period, the dilute polymer solution (0.5%) was introduced, the reactor was sealed and charged with hydrogen.

A number of exploratory hydrogenations were conducted and experimental details were established. Whereas some workers reported successful hydrogenation in cyclohexane at 50 °C, we found it was necessary to use decalin at 100 °C. Apparently, our samples of *PDMB* did not dissolve completely in cyclohexane which suggests that they might have had higher molecular weight than those previously employed. If hydrogenations were carried out on samples of *PDMB* that had not completely dissolved, the product was sometimes isolated without evidence of much hydrogenation.

Previous reports described successful polymer isolation by a simple washing with dilute acid followed by precipitation in methanol. We had to use several reprecipitations of the polymer from hot decalin into an isopropanol/10% concentrated HCl solution, otherwise catalyst residues remained in the hydrogenated polymer.

A change of about 30% in the inherent viscosity was observed after homogeneous hydrogenation (Table 1). For the heterogeneous hydrogenation, however, the numeric value of the inherent viscosity was lowered by nearly 0.6 dL/g, indicating considerable decrease in molecular weight. This seemed to be caused by the necessity of using severe conditions for the hydrogenation, which caused hydrogenolysis of the polymer.

The mechanism of hydrogen addition to double bonds of polymers with soluble transition metal compound catalysts derived from cobalt and organometallic compounds[22] is not stereospecific although numerous catalyst systems have proven successful for hydrogenation. A thorough evaluation of all catalyst systems must be completed before a general mechanism can be postulated. It seems that the first step in the reaction for the preparation of the hydrogenation catalyst involves the combination of the trialkylaluminium with the transition metal salt to form an organo transition metal compound[26]. Reaction of this salt with hydrogen forms a transition metal hydride which then adds across the olefin double bond. The final step, reaction with hydrogen, produces the hydrogenated product and regenerates the active catalyst.

C. Investigation of the Mode of Hydrogen Addition

In *H-H PP* two ethylidene groups are linked next to each other in the polymer chain (separated by two methylene groups), either by a *threo*- or *erythro* linkage. Hydrogenation of *cis* or *trans*-1,4-*PDMB* could generate these two isomers; the *threo* or *erythro* form. Assuming that *cis* addition of hydrogen to *cis-PDMB* occurs, the *erythro* structure in the polymer would be generated. *Cis* addition to *trans*-1,4-*PDMB* would give the *threo* structure of *H-H PP* (Equation 4).

Analysis of the product obtained by homogeneous catalytic hydrogenation of either pure *cis* or pure *trans*-1,4-*PDMB* by ^{13}C-NMR indicated that *cis* addition of hydrogen predominated, but was not exclusive. Fig. 1 shows a typical ^{13}C-NMR spectrum for the *erythro* structure predominating polymer and the *threo* predominating *H-H PP* with the assignments for the various carbon atoms (Table 3) made according to earlier studies[27, 28, 6].

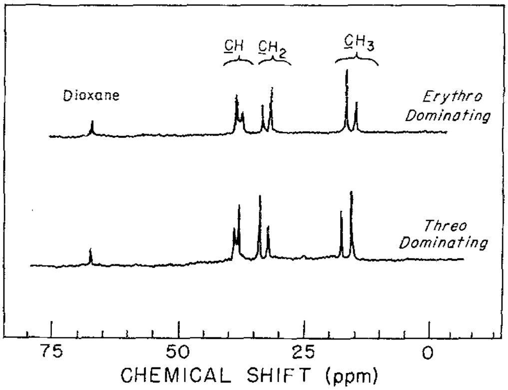


Fig. 1. ^{13}C-NMR Spectra of *erythro* and *threo*-predominating *H-H* polypropylene

Recently it was shown[29] that the relative intensity distribution of methyl resonances of *PP* in the ^{13}C-NMR spectrum can be used reliably to make quantitative estimates of the configuration of individual units in the polymer. It was shown experimentally that an equal *Overhauser* effect was observed for each of the ^{13}C methyl resonances in *PP*. The work of *Prudhomme*[30] confirmed that the ^{13}C-NMR analysis could be applied for quantitative assignments of the intensities to both hydrogenation products of polyisoprene and *PDMB*. With this in mind, quantitative analysis of the microstructure of our *H-H PP* was carried out (Table 3).

H-H PP from hydrogenation of *cis*-1,4-*PDMB*, has about 65-70% *erythro* linkages. Hydrogenated *trans*-1,4-*PDMB* shows a level of 65% of the *threo* configurations. Recalling Equation (4), it is apparent that *cis* addition predominates in the course of our hydrogenation, but is not exclusive even though exclusive hydrogen *cis* addition has been recognized for many heterogeneous hydrogenations[31] of low molecular weight compounds. For comparison of our experiments on the homogeneous hydrogenation of 1,4-*PDMB*, *cis*-1,4-*PDMB* was also hydrogenated with a Pd/carbon catalyst. After 24 hours at 1000 p.s.i. (H_2 pressure) and 130 °C, *H-H PP* was recovered in less than 50% yield. Several filtrations of the reaction solution were necessary to completely remove all catalyst residue; these operations account for much of the material loss. *Cis* addition was again found to predominate at approximately the same levels found with homogeneous catalysts.

D. Characterization of H-H Polypropylene

Spectral properties. Infrared spectra of all *H-H PP* samples were very similar. Strong bands were observed from 2960 to 2850 cm^{-1} (ν_{as}, —CH_3, ν_a; —CH_2 and ν_s, —CH_3) and at 1460 and 1380 cm^{-1} (δ_{as}, —CH_3 and δ_s, —CH_3). Adsorptions of medium intensity were observed in the fingerprint region at 1130, 1035 and 745 cm^{-1}. It is known that in the spectrum of crystalline, isotactic polypropylene a sharp doublet appears at 995 and 974 cm^{-1} (Ref. [32, 33]) which was not found in amorphous *H-H PP*.

In Fig. 2 and Table 2 are compared the ^{13}C-NMR spectral values of isotactic *H-T*, atactic *H-T* and *H-H PP*. The peak assignments for isotactic and atactic polypropylene are in good agreement with the results obtained by other workers[34]. It is interesting to note the effect of configuration of the ethylidene groups on the chemical shifts of *H-H PP*. The methylene and methyl carbons are shifted to both higher fields for the *H-H* polymer as compared to the *H-T* polymer (Table 3 and Fig. 2).

Model compounds of *PP* containing both *H-H* and *H-T* arrangements of monomer units have been synthesized earlier[35]. The ^{13}C-NMR spectra have been assigned and revealed that chemical shifts of the methyl groups in the chain are influenced by two factors: (1) The presence of another methyl group in the α-position (*H-H* linkage) had the general effect of a shift to higher field. (2) An additional shift to high field for an α-methyl group of the threo configuration was observed. These same authors prepared an empirical relationship for predicting the ^{13}C methyl shift, based on structure and configuration.

Data in Table 3 show that the methyl group in *H-H PP* has chemical shift values as expected from model compound studies.

Wide-Angle X-Ray Studies. Isotactic *H-T*, atactic *H-T* and *H-H PP* were investigated by X-ray diffraction. Fig. 3 shows the *Debye-Scherrer*

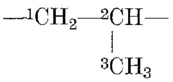
Table 2. *Chemical shift data*[a] *of* ^{13}C-*NMR spectra*[b] *of atactic, isotactic H-T and H-H polypropylene*

Carbon[c] No.	Atactic[d] *PP*, ppm	Isotactic *PP*, ppm	*H-H PP* ppm[e]
1	47.16 (9)		33.55 (*t*)
	46.57 (22)	46.53	31.88 (*e*)
2			38.73 (*e*)
	28.88 (16)	28.88 (5)	37.86 (*t*)
	28.50 (24)	28.54 (3)	
3	21.98 (13)	21.98	
	21.13 (6)		
	21.01 (6)		17.15 (*e*)
	20.42 (6)		15.20 (*t*)

[a] Relative to dioxane at 67.39. Numbers in parentheses indicate relative intensity.

[b] Measured at 90 °C in *o*-dichlorobenzene.

[c] Carbon numbers as follows:



$$—{}^{1}CH_2—{}^{2}CH(—{}^{3}CH_3)—$$

[d] Estimated to be 50% isotactic, 25% syndiotactic and 25% heterotactic.

[e] *e* = *erythro; t* = *threo.*

Table 3. *Chemical shift data*[a] *and relative intensity in the* ^{13}C-*NMR spectrum*[b] *of typical samples of H-H polypropylene*

Type of Carbon Atoms		Chemical Shift		Relative Intensity	
		erythro	*threo*	*erythro*	*threo*
Hydrogenated *cis-PDMB*	CH	38.73	37.86	5	3
	CH_2	31.88	33.55	5	3
	CH_3	17.15	15.20	7	3
Hydrogenated *trans-PDMB*	CH	38.71	37.87	4	7
	CH_2	31.84	33.54	4	9
	CH_3	17.13	15.22	6	8

[a] Relative to dioxane at 67.39 ppm.

[b] Measured at 90 °C in *o*-dichlorobenzene.

diagrams of these three polymer samples and Table 4 lists the calculated "d" spacings from these diagrams. It can be seen that isotactic *PP* showed several sharp rings of strong intensity. Our atactic *PP* did suggest the presence of some crystallinity. In comparison, *H-H*

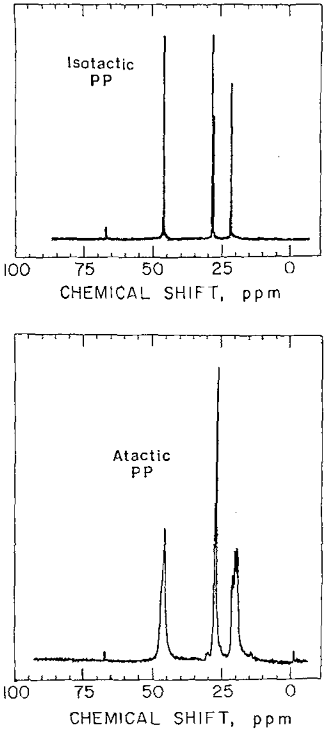


Fig. 2. ^{13}C-NMR Spectra of isotactic *H-T*, atactic *H-T* and *H-H* polypropylene

Table 4. *Wide-angle X-ray studies: interplanar spacings of isotactic, atactic H-T and H-H polypropylene*

Isotactic *H-T PP*		Atactic *H-T PP*		*H-H PP*	
Spacing	Relative Intensity	Spacing	Relative Intensity	Spacing	Relative Intensity
				7.15	Diffuse
		5.49	w	5.49	Diffuse
		2.99	s	2.99	Diffuse
2.61	s				
2.49	m	2.49	m		
		2.33	w		
2.17	s				
2.04	s	2.11	w		
1.77	w	1.97	w		
1.70	w				

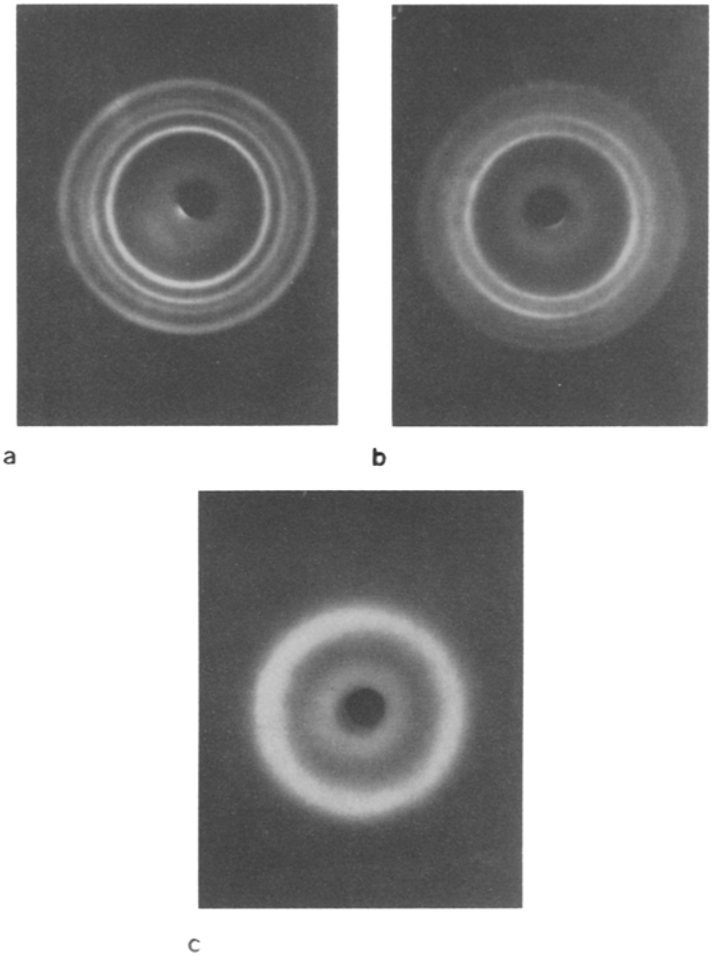


Fig. 3. Wide-angle X-ray diagrams of polypropylenes: *a* Isotactic *H-T*, *b* Atactic *H-T*, *c* *H-H*

PP gave only three diffuse amorphous rings common for all *H-H* polymer samples.

Glass Transition Behavior. PP samples were studied by DSC; of particular interest were the differences in the actual temperature of the transition points of individual polymers. *Trans*-1,4-*PDMB* had a T_g 12 °C, and after hydrogenation a T_g of *H-H PP* of —30 °C (Fig. 4) was observed. *Cis*-1,4-*PDMB* had a T_g at 4 °C, the hydrogenated (*H-H PP*) polymer showed a T_g of about —40 °C.

This result is very intriguing in light of some other T_g measurements for hydrogenated-1,4-*PDMB*'s (*H-H PP*). *Prudhomme*[6] found that the hydrogenation of 74% *trans*-1,4, 23% *cis*-1,4 and 3% 1,2-*PDMB* gave a threo predominating *H-H PP* with a T_g of about —25 °C. *Cowie*[5], referring to his sample of *PDMB* as predominantly *trans*-1,4 with about 6% 1,2 units in the chain, extrapolated a value of —10 °C for *H-H PP* after hydrogenation. However, *Cowie* used *p*-toluene sulfonyl hydrazide (*TSH*) as the reducing agent. A number of reductions were found necessary to reduce unsaturation to less than 10%. As discussed earlier, the combination of a relatively high concentration of 1,2-linkages and residual unsaturation raises doubt about the structural purity of the *H-H* polymer samples.

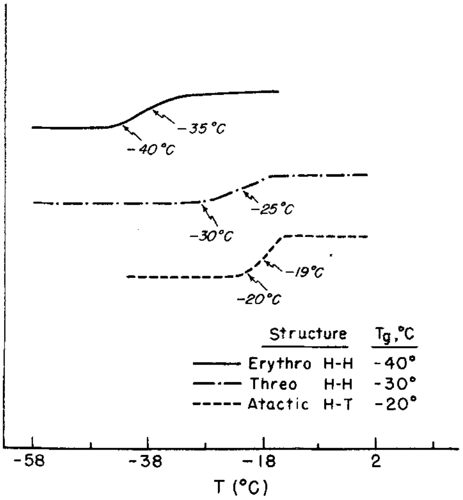


Fig. 4. DSC Scans of atactic *H-T* and *H-H* polypropylenes

The values of T_g of *trans*-1,4-*PDMB* (12 °C) after hydrogenation were found to be lower, —30 °C, which is approximately the same as that reported by *Prudhomme*. Our *erythro* predominating structure, however, showed a T_g of —40 °C.

Karasz and *MacKnight*[36] have considered the influence of tacticity on the T_g in mono and di-substituted vinyl polymers. They concluded that no difference in the T_g should be detected in mono-substituted polymers such as *PP*. Extensive studies on the T_g of stereoblock isotactic and atactic *PP*[8] have indicated a small difference in T_g of atactic and isotactic samples, but this was attributed to a function of molecular order, not steric configuration. The

Table 5. *Values of T_g quoted for atactic and isotactic H-T polypropylene*

Steric Configuration	Measuring Technique	T_g, °C	$10^{-5} M_v$
Isotactic	—	—35	—
Atactic	—	—35	—
Isotactic	Heat	—13	—
Atactic	Capacity	—24	—
Atactic	T.M.A.[a]	—17	Unfractionated
Atactic	D.T.A.[b]	—18	0.059
Atactic	D.T.A.	—8	5.0
Isotactic	Dilatometry	—5[d]	—
Atactic	Dilatometry	—15[d]	—
Isotactic	Heat	—6	1.4
Atactic	Capacity	—14	0.157
Isotactic (annealed)	T.P.[c]	—5.5	1.14
Isotactic (quenched)	T.P.	—2	1.14
Atactic	T.P.	—5	—
Isotactic	DSC	—1	3.2
Atactic	DSC	—7	0.64
Stereoblock	DSC	—7	0.3
Isotactic	T.P.	0	—
Atactic	T.P.	0	—
Isotactic	NMR	12	—
Atactic	NMR	—3	—
Isotactic	Audio Frequency	27	20.0
Atactic	(0-2000 Hz)	—3	3.0

[a] T.M.A. = Thermomechanical analysis.
[b] D.T.A. = Differential Thermal analysis.
[c] T.P. = Torsional pendulum.
[d] Average of the lower of two observed transitions.

observed differences in T_g of *erythro* and *threo* predominating *H-H PP* samples could be an example of a similar effect. The lower T_g of *H-H PP* as compared to *H-T* polymer is consistent with the earlier reports that bulky side groups in the *H-T* position of nonpolar polymers cause a more significant stiffening effect on the polymer chain.

It has long been known that the value of T_g of a polymer depends on the type of measurement, but it should be remembered that the stereochemistry is often not known. *PP* is an excellent example of this phenomenon; Table 5 shows a variety of values observed for different types of measurements.

Dynamic mechanical measurements were also carried out by us on both atactic *H-T* and *H-H PP*. Fig. 5 shows both the change in storage modulus (E′) and loss modulus (E″) observed for these polymers. This method of measurement showed the T_g of atactic *H-T* polymer to be —10 °C. DSC studies of the

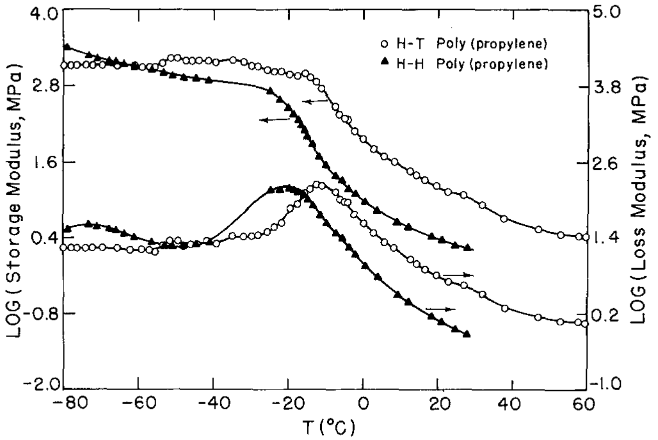


Fig. 5. Dynamic mechanical studies of atactic *H-T* polypropylene and *H-H* polypropylene

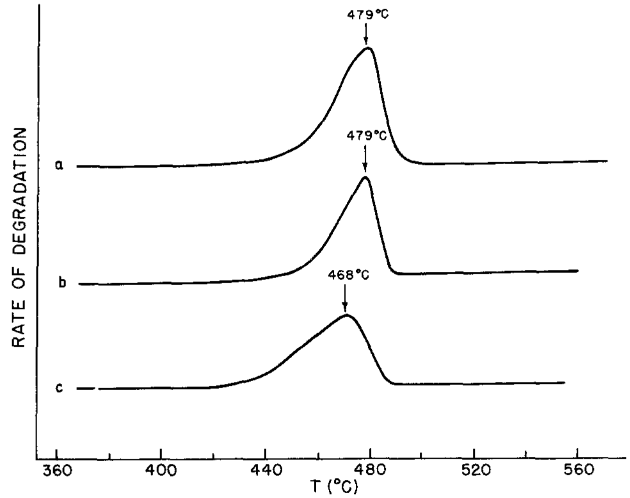


Fig. 6. DTG Scans of polypropylenes: *a* Atactic *H-T*, *b* Isotactic *H-T*, *c H-H*. Heating rate 20 °C/min under nitrogen

same sample indicated a T_g of —20 °C. The T_g of the *H-H* polymer (DSC, T_g = —30 °C) was found by Rheovibron studies to be —20 °C. The dynamic mechanical testing confirms the lower T_g for *H-H PP* as compared to the atactic *H-T* polymer.

Thermal Stability of the Polymers. Thermal degradation behavior of *H-H PP* and *H-T* (atactic and isotactic) *PP* was investigated (Fig. 6) and compared. Table 6 summarizes the thermal degradation behavior of all the polymers prepared in this study. The degradation behavior of *H-H PP* is very similar to that of atactic and isotactic *H-T PP*. A lower degradation temperature for *PDMB* typical for all butadiene polymers was observed which is not unusual because of the ease of forming allyl radicals by cleavage of the single bond of low dissociation energy between the two allylic methylene groups.

Table 6. *Thermal degradation of cis and trans-1,4-poly(2,3-dimethylbutadienes) and polypropylenes*

Polymer[a]	DTG-Max. Degradation Temp., °C	TGA Initial Degradation Temp., °C
cis-1,4-poly(2,3-dimethylbutadiene)	380	281
trans-1,4-poly(2,3-dimethylbutadiene)	383	280
Atactic polypropylene	479	338
Isotactic polypropylene	479	342
H-H polypropylene	468	341

[a] Sample size 15-20 mg; heating rate 20 °C/min under nitrogen.

The results of our study on the thermal stability of the *PP* are consistent with recent suggestions that *H-H* and *H-T* polymers have similar temperatures of maximum rate of degradation as long as hydrogen is the fourth substituent on the substituted carbon atoms and no group larger than hydrogen is a substituent in the beta-position[37].

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