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Elastomeric Polypropylenes from Alumina-Supported Tetraalkyl Group IVB Catalysts. 1. Synthesis and Properties of High Molecular Weight Stereoblock Homopolymers

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ABSTRACT: A new family of high molecular weight stereoblock polypropylenes has been prepared by homopolymerization of propylene with highly active catalysts consisting of metal oxide supported group IVB transition-metal compounds of the type R_4M (M = Ti, Zr, Hf; R = benzyl, neopentyl, neophyl). With appropriate selection of catalyst and conditions, polypropylenes covering a wide range of physical properties from low modulus thermoplastic elastomers to flexible plastics can be synthesized. Novel homopolymers in the lower range of isotactic content and crystallinity are designated elastomeric polypropylene (ELPP). The elasticity is attributed to a high molecular weight ether-soluble fraction, which can cocrystallize with more stereoregular components to form a cross-linked network.

Introduction

Since the pioneering advances of Natta et al.,[1-3] it is well established that polypropylenes prepared with Ziegler-type coordination catalysts consist of different stereoisomers that can be effectively separated by extraction with boiling solvents. Isotactic polypropylene is the highly crystalline fraction that is insoluble in boiling heptane; amorphous and low crystallinity polypropylenes can be extracted by boiling ether. During the last decade, major advances have been made in catalysts for isotactic polypropylene. Current high yield/high stereospecific magnesium chloride supported titanium chloride catalysts provide excellent steric control. Low stereospecific centers responsible for the formation of stereoirregular polypropylenes have been successfully eliminated by selective poisoning.[4-14]

The synthesis and properties of polypropylenes with lower levels of stereoregularity have been given much less attention. Polypropylenes in which there is a completely random arrangement of the methyl groups have been prepared by the palladium-catalyzed isomerization of isotactic polypropylene[15] and by direct polymerization with soluble zirconium catalysts.[16-21] These and other catalysts producing a wide range of random to stereoblock character have been reported in recent symposia.[22-24]

Natta et al. identified a new class of stereoblock polypropylene elastomers by fractionating polypropylenes made with conventional titanium- and vanadium-based catalysts.[1-3] Several research groups attempted the synthesis of elastomeric stereoblock polypropylenes or polyolefins but did not develop a practical process.[25-27] Not only were catalyst productivities low, requiring subsequent catalyst removal, but only a portion of the polymer had the desired properties, requiring removal of the highly isotactic fractions to leave an elastomeric product.

We report here the high-yield synthesis of novel stereoblock polypropylenes that possess elastomeric properties, as polymerized, and that can be blended with isotactic polypropylene to obtain a wide range of physical properties.[28-31] We demonstrate that the key component responsible for the elasticity is a high molecular weight ether-soluble fraction that can cocrystallize with more stereoregular components to form a cross-linked network. In the accompanying paper,[32] we further verify this hypothesis by characterizations of the chain microstructure, crystallization behavior, and morphology of typical ELPPs.

Our interest was stimulated by the discovery that certain single-component organotransition-metal catalysts supported on metal oxide produced stereoblock polypropylenes of low crystallinity and high elasticity. These catalysts were made by reacting transition-metal alkyls R_4M (where M is Ti, Zr, or Hf and R is an alkyl with no β-hydrogens) with Al_2O_3. Earlier work had shown that these transition-metal alkyls alone were relatively inactive for olefin polymerization and produced only small amounts of predominantly isotactic polypropylene in the presence[33-35] or in the absence[14,36] of additional aluminum alkyl. Ballard[37-43] showed that the lifetime and catalyst efficiencies were dramatically increased when the transition-metal alkyl was supported on the surface of a metal oxide such as Al_2O_3. Propylene polymerization rates were low and the product contained about 30% of a toluene-soluble fraction;[42] no further characterization of these irregular polypropylenes has been reported.

In our research on stereoblock polypropylenes, we used the support technology developed by Setterquist et al.,[44-49] who found that nonporous alumina with a fundamental particle size of 10–20 nm and a surface area >100 m^2/g gave greatly improved catalyst performance, particularly for the polymerization of ethylene at high temperatures.[48,49] They also found that the catalyst gave very broad molecular weight distributions, which they related to the presence of different catalyst sites. Firment found four different kinds of OH on the surface and identified at least three spectroscopically different types of zirconium.[50]

Experimental Section

Catalyst Preparation. All equipment was dried and maintained under a nitrogen atmosphere. All materials were handled and stored in a Vacuum Atmosphere drybox which was continuously purified with the HE-493 Dritrain.

The catalysts consisted of group IVB metal alkyls, R_4M, supported on Al_2O_3, where M was Ti, Zr, or Hf and R was $PhCH_2$, $(CH_3)_3C$, $PhC(CH_3)_2C$, or BH_4. The metal alkyls and metal oxide supported catalysts were prepared by the procedures of Setterquist et al.[44-49] Fumed nonporous alumina (Alumina C, Degussa Co., Germany) was dried in a nitrogen stream at 850 °C for at least 4 h and then rehydrated at 25 °C and 50% relative humidity for 16 h. This alumina, containing 3–5% water, was heated at 400–450 °C for at least 4 h in a sweep of dry nitrogen to produce material containing about 0.8% water (0.4–0.8 mmol of hydroxyl/g of

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Al_2O_3). The surface area usually was about 100–150 m^2/g.

The catalysts generally were prepared by stirring 0.2–0.6 mmol of the organometallic compound with 1–2 g of dry Degussa alumina suspended in 40–60 mL of cyclohexane for at least 1 h, or preferably overnight. For preparation of the hydrides, the catalyst was pretreated with H_2, generally for 20 min, at temperatures from ambient to 150 °C.[44,48] Then the catalyst was transferred to the polymerization reactor either via a 75-mL stainless steel cylinder or by a syringe. All operations were conducted with a nitrogen purge or blanket.

A more stereospecific magnesium chloride supported titanium catalyst was prepared for comparison of polymerizations and products. Anhydrous $MgCl_2$ (15 g) was ground with $TiCl_4$ (2 g) in a ball mill for 18 h, followed by repeated washing with dry heptane and drying overnight at high vacuum. The $MgCl_2/TiCl_4$ catalyst (2.46% titanium content) was activated by addition of triethyl aluminum (Al/Ti molar ratio of about 100).

Polymerization. Propylene was polymerized in bulk or hydrocarbon diluent. The 1-L stainless steel autoclave was dried by heating at 150 °C for 4 h while being purged with dry nitrogen. For polymerization in liquid propylene, the reactor was evacuated, cooled, and charged with 168 g of propylene. After the system had warmed to 25 °C, hydrogen was added to the desired partial pressure, and the catalyst suspension was injected from a blow case to start the polymerization. The desired reaction temperature was maintained constant by heating or cooling with an internal coil. Reaction temperatures were varied from ambient to 150 °C and residence times from a few minutes to several hours.

In a solvent polymerization, 450 mL of cyclohexane, dried by passing through a 3-in. bed of Woelm acid alumina into a storage container, was injected into the reactor through syringe needles under nitrogen pressure and nitrogen countercurrent from the reactor port. Then 126 g of propylene and the desired partial pressure of hydrogen were added, and the polymerization was started by injecting the catalyst suspension.

The polymer obtained was usually a viscous gel. It was stirred in a Waring blender with 1 L of acetone containing 0.3 g of Irganox 1010 antioxidant, followed by filtration and drying in a vacuum oven at 70–80 °C for at least 4 h.

For the comparison between the single-component catalyst and the high-activity magnesium chloride supported catalysts, propylene was polymerized in 400 mL of dry heptane in a 750-mL glass reactor at 45 psi propylene pressure and 65 °C for 1 h.

Hercules, Inc., Profax 6523 and Afax, commercial crystalline and atactic polypropylenes, were obtained and used in testing and characterization of blends.

Polymer Fractionation. The diastereoisomers of polypropylene were separated by extractions with boiling solvents, usually diethyl ether and then hexane or heptane. The extractions were conducted on 2-g samples in Kumagawa extractors[2] under nitrogen at the boiling temperatures of the solvents for at least 15 h and until ≤0.01 g weight loss was observed overnight. (Some extractions were conducted on larger samples in standard unjacketed Soxhlet extractors, for which the extraction temperatures were probably somewhat lower, but with results similar to those for the smaller fractionations.) The soluble polymers were isolated by precipitation in methanol, filtration, and drying in a vacuum oven at 70–80 °C overnight.

Polymer Characterization. The inherent viscosities were determined on solutions of polymer in decahydronaphthalene containing 0.1 g/L of 2,6-di*tert*-butyl-4-methylphenol (BHT) at 135 °C in a Cannon-Ubbelhode viscosimeter. $\eta_{inh} = \ln (T/T_0)/c$, where T and T_0 are the efflux time of the solution and solvent, respectively, c is the concentration, usually 0.05 g/dL, and η_{inh} is in units of deciliters per gram.

The molecular weight distributions were measured on a Waters 150C chromatograph with a Shodex AT80M/S column operating at 135 °C with 1,3,5-trichlorobenene as the solvent. Polystyrene was used as the primary standard.

Melting points and heats of fusion were determined by differential scanning calorimetry using a Du Pont thermal analyzer. The DSC scans were obtained by first heating from 40 to 200 °C at a rate of 20 °C/min, cooling from 200 to 40 °C at the same rate, and then reheating from 40 to 200 °C at 10 °C/min. All the DSC values in the tables are reheat values. The heat of fusion of 100% crystalline polypropylene ΔH_f = 209 J/g was used in calculating percent crystallinity.[51]

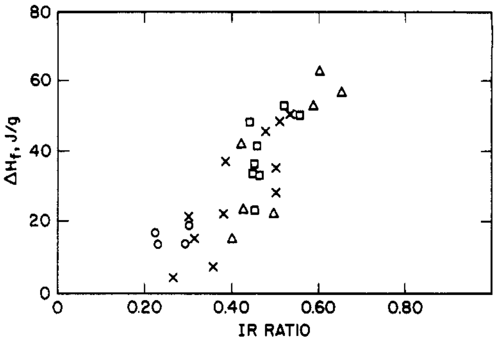

Figure 1. Heat of fusion versus IR ratio for stereoblock polypropylenes from R_4M/Al_2O_3 catalysts. R: (○) neopentyl; (×) neophyl; (□) neophyl (catalyst twice recrystallized); (△) benzyl.

X-ray diffraction patterns of the specimens were obtained on a scanning diffractometer with Ni-filtered Cu Kα radiation. Crystallinity was calculated from the areas under the crystalline peaks versus the total scattering.

Density crystallinity was measured by a buoyancy method with methanol as the buoyant medium. Five replicate measurements were made for each sample. The results were corrected for residual alumina catalyst determined by ashing the samples at 800 °C for 2 h. Densities of crystalline polypropylene, amorphous polypropylene, and alumina were taken as 0.938, 0.852, and 3.97 g/cm^3, respectively.

Infrared spectra were obtained by transmission on melt-pressed films using a Nicolet FTIR spectrometer. The IR ratio = A_{993}/A_{975}, calculated from the absorptivities at 993 and 975 cm^{-1}, is a measure of the isotactic helix content.[52] The inverse of the ratio used by Luongo was employed because it correlated linearly with estimates of crystallinity by DSC, X-ray diffraction, and density measurements.

Test specimens were prepared by hot compression molding the polymer at 180 °C and 20000 psi (276 MPa). Tensile and stress–strain measurements were carried out on straight or dumbbell specimens 0.25 in. (0.64 cm) wide and 0.018–0.080 in. (0.045–0.20 cm) thick according to ASTM Method D412.

The tensile set was determined by elongating the specimen 20 in. (51 cm)/min to 300% elongation and then immediately reversing at the same rate until the specimen was at zero stress, all at 23 °C. The tensile set = 100 × $(l_f - l_i)/l_i$, where l_i and l_f were the initial and final length, respectively, between bench marks on the sample.

Hysteresis curves were run in the same manner but with additional cycles to 500 and 700% elongation and a final elongation to break.

Dynamic mechanical spectra were obtained on melt-pressed slabs with a Du Pont dynamic mechanical analyzer.

Results and Discussion

Catalyst efficiencies were generally high, ranging up to 600 g/mM R_4M (or ca. 6 × 10^5 g/mol of transition metal). The polymers produced by these catalysts were high molecular weight semicrystalline stereoblock polypropylenes. The isotactic content ranged from 20 to 70% and the heat of fusion, ΔH_f, from 10 to 70 J/g (Figure 1). In contrast, typical commercial crystalline polypropylenes have >90% isotacticity and ΔH_f ca. 100 J/g.

Stereoregularity. The degree of stereoregularity, as indicated by the IR ratio, depends on the transition metal and the ligand. Some of the results obtained with various catalyst systems are summarized in Table I. Figure 2 shows the ranges of stereoregularity obtained with supported Ti, Zr, and Hf alkyls, used directly or after prehydrogenation to form the hydrido catalyst. Titanium gives the highest isotacticities. Bulky ligands, such as neopentyl or neophyl (2-methyl-2-phenylpropyl), give lower isotacticities than benzyl. We speculate that these bulky ligands favor reaction with the more exposed surface hy-

Table I
Propylene Polymerizations with R_4M/Al_2O_3 Catalyst[a]

catal components		concn, mM/g of Al_2O_3	yield, g/mM R_4M	η_{inh}, dL/g	IR ratio[b]	T_m, °C	ΔH_f, J/g	% ether soluble
M	R							
Zr	benzyl	0.3	83	13.2	0.40	148	15.0	
		0.3[c]	146	3.8	0.46	154	44.3	
		0.4[d]	165	4.0	0.53	155	48.1	41
Zr	neophyl	0.2[d]	525	3.1	0.46	149	23.0	54
		0.3[d]	373	3.4	0.48	153		
		0.6[d]	123	3.6	0.55	155	50.1	42
		0.5	148	8.7	0.57	153	56.4	
Zr	neopentyl[g]	0.15	234	14.3	0.30	144	18.8	
		0.6	115	11.3	0.52	153	41.0	
ZrCl	neophyl	0.2	85	7.6	0.31	146	15.4	53
$Zr(BH_4)_4$		0.5	34	6.2	0.55	159	54.3	
Ti	benzyl	0.15[e]	284	11.0	0.56	150	55.6	
		0.3[e]	262	10.1	0.53	150	29.3	34
		0.2[d]	140	6.7	0.60	151	68.1	45
Ti	neophyl	0.15$_d$	180	7.4	0.53	150	60.2	37
		0.3[d]	150	5.9	0.56	147	70.2	37
		0.2[e]	290	8.0	0.56	153	41.8	
Hf	neophyl	0.3[d]	226	10.6	0.44	150	45.1	31
		0.3[e]	316	8.9	0.37	150	29.7	51
		0.3[f]	137	8.2	0.48	154	46.4	39

[a] Polymerization in liquid propylene 1 h at 50 °C using 1 g of Al_2O_3 catalyst support. [b] A_{993} (cm^{-1})/A_{975} (cm^{-1}). [c] Catalyst prehydrogenated 20 min at 150 °C; 40 psi of H_2 during polymerization. [d] 40 psi of H_2 during polymerization. [e] Catalyst prehydrogenated 20 min at 25 °C, 40 psi of H_2 during polymerization. [f] 25 psi of H_2 during polymerization. [g] Composition R_3ZrCl.

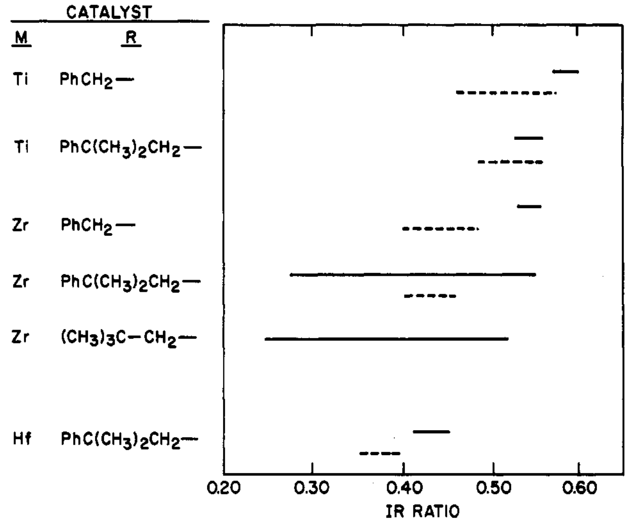

Figure 2. IR ratio (isotacticity) ranges for R_4M/Al_2O_3 catalysts. (—) R_4M/Al_2O_3; (---) $R_4M/Al_2O_3/H_2$.

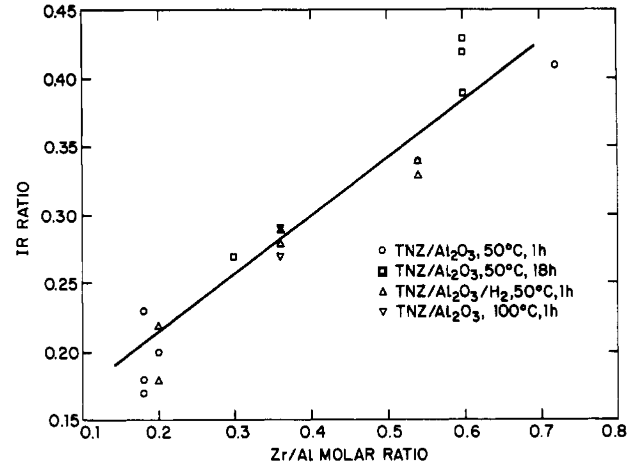

Figure 3. IR ratio (isotacticity) as a function of the Zr/Al ratio for TNZ/Al_2O_3 catalysts.

Table II
Propylene Polymerization with TNZ/Al_2O: Effect of Aluminum Alkyls[a]

TNZ, mM/g of Al_2O_3	0.2	0.2	0.3
i-Bu_3Al, mM/g of Al_2O_3		0.2	
i-$BuAl_2AlH$, mM/g of Al_2O_3			0.3
yield, g/mM TNZ	585	185	153
η_{inh}, dL/g	3.42	3.22	4.36
IR ratio	0.46	0.56	0.54
T_m, °C	150	156	156
ΔH_f, J/g	23.0	55.6	50.2

[a] Polymerizations of liquid propylene with TNZ/Al_2O_3, 40 psi of H_2, 50 °C.

droxyls, so that the catalyst site has fewer steric restrictions. Similarly, hydrogenated catalysts all give lower isotactic contents; this is consistent with the hydride providing a less sterically hindered site.

TNZ–Al_2O_3 Catalyst. Some of the catalysts, such as the tetraneophylzirconium (TNZ) and tetraneopentylzirconium on alumina, make a wide range of isotacticities. In these systems, the stereoregulation was strongly dependent on the concentration of the metal on the surface or the Zr/Al_2O_3 ratio. As shown in Figure 3 the isotactic content increases as the Zr/Al_2O_3 ratio increases; catalyst efficiency decreases at the same time. Firment[50] showed that the alumina sites become saturated at about 0.2 mm of Zr/g. This suggests that above a certain level, excess Zirconium alkyl complexes with the Zr alkyls on the surface, reducing their activity and increasing the stereoselectivity.

Similar effects are found on addition of aluminum alkyls. Table II shows that the addition of stoichiometric amounts of triisobutylaluminum or diisobutylaluminum hydride increases isotacticity, crystallinity, and melting point and reduces the yield. If R_3Al/Zr is >1, the yield of polymer drops drastically. Strong electron donors such as esters are potent catalyst poisons; this is not surprising, as the catalyst has no aluminum alkyl present to complex or react with such donors.

Hydrogen is both a chain-transfer agent and a catalyst modifier with the TNZ/Al_2O_3 catalyst. This is best shown by a comparison of this catalyst with a high-efficiency $MgCl_2/TiCl_4/AlEt_3$ catalyst (Table III). The latter catalyst was not modified with donors, so as to provide

Table III
Comparison of Propylene Polymerizations[a]

catalyst	yield[d]	fraction	%	η_{inh}, dL/g	T_g,[e] °C	T_m,[e] °C	ΔH_f,[e] J/g	M_n	$M_w \times 10^3$	M_w/M_n
TNZ/Al_2O_3[b]	47.7	total	100.0	10.2	−10.1	147.1	13.1	75.5	600	8.0
		ether sol.	28.2	3.81	−8.0	52.0	1.6	80.8	604	7.5
		hept sol.	17.9	4.78	−7.8	130.2	27.7	39.3	934	23.9
		hept insol	50.0	15.3	−7.4	147.7	49.0	455	2626	5.8
TNZ/Al_2O_3[b] + 5 psi of H_2	92.7	total	100.0	4.08	−11.5	151.8	5.0	34.0	370	10.9
		ether sol.	49.0	2.54	−8.8	53.0	1.8	22.3	261	11.7
		hept sol.	33.0	3.28	−10.1	137.0	29.2	22.0	478	21.6
		hept insol	24.0	8.04	−7.5	149.9	68.7	108	3460	3.2
$MgCl_2/TiCl_4/AlEt_3$[c]	2680	total	100.0	2.11	−394	159.6	62.5	22.4	128	5.6
		ether sol.	21.0	0.82	−3.6	nd	nd	19.1	66.8	3.5
		hept sol.	19.3	0.78	−1.6	140.1	63.0	28.0	110	3.7
		hept insol	53.0	3.45	nd	166.3	102.0	160	531	3.0
$MgCl_2/TiCl_4/AlEt_3$[c] + 5 psi of H_2	2140	total	100.0	0.53	−9.8	159.0	78.2	12.1	42.3	3.5
		ether sol.	26.6	0.31	−10.4	nd	nd	6.7	16.5	2.5
		hept sol.	24.5	0.28	−1.8	156.4	63.5	10.0	26.7	2.7
		hept insol	45.7	0.83	nd	161.3	105.0	26.8	110	4.1

[a] Propylene was polymerized in *n*-heptane at 60–65 °C for 1 h. [b] 200 mg of tetraneophylzirconium (TNZ) supported on 1 g of dry Degussa Alumina C. [c] 45 mg of $MgCl_2/TiCl_4$ (2.61% Ti) activated with 2 mL of $AlEt_3$. [d] g/mmol of M. [e] nd, not detected or very weak.

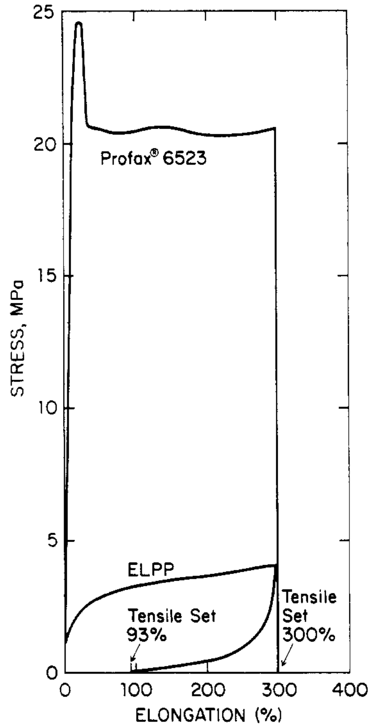

Figure 4. Stress–strain and tensile set behavior of Hercules Profax 6523 (highly isotactic) polypropylene and an ELPP. The strain and recovery rate was 20 in./min (51 cm/min), the rate normally used to characterize elastomers.

polymers of lower stereospecificity, similar to those from the zirconium catalyst.

With the TNZ catalyst, hydrogen doubles the catalyst efficiency and lowers the crystallinity. Fractionation shows that the latter is due to an increase in the ether fraction from 28% to 49% and the heptane-soluble fraction from 18% to 33%. The molecular weights of these two fractions are only slightly lower. This implies that while hydrogen is a moderate chain-transfer agent, it has either greatly activated the less stereoregular catalyst sites or reduced the stereospecificity of the other sites.

The titanium catalyst is 20–50 times more active than the zirconium catalyst under the experimental conditions. In the presence of hydrogen, however, the efficiency of the titanium catalysts decreases about 20%, while the crystallinity increases. The fraction of less crystalline material (the ether and heptane extracts) increased only from 40% to 50%. Further, both of these fractions had very low molecular weights (η_{inh} < 1) with or without hydrogen. These low molecular weights are consistent with the known propensity of the nonstereospecific sites in titanium chloride catalysts to chain transfer. Finally, in contrast to polymers from the TNZ catalyst, the ether-soluble fraction had no measurable crystallinity.

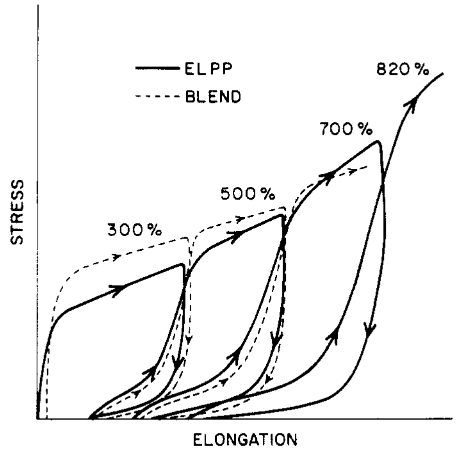

Figure 5. Hysteresis curves of an ELPP (η_{inh} = 5.5) and a milled blend (η_{inh} = 3.9) of its ether-soluble and hexane-insoluble fractions in their proportions in the whole polymer: ether soluble, 47%, η_{inh} = 2.5; hexane insoluble, 29%, η_{inh} = 8.9. The specimens were elongated and returned to zero stress at a strain rate of 51 cm/min on successive cycles to 300%, 500%, 700%, and elongation to break.

Polymer Properties. The most distinguishing feature of these polypropylenes is their elastic behavior. In sharp contrast to highly crystalline polypropylene, the polymers had typical properties of a thermoplastic elastomer in stress–strain measurements, i.e., they showed no plastic yield and had elastic recovery. These elastomeric polypropylenes have been designated ELPP.

Figure 4 shows the stress–strain curves of ELPP and of Hercules Profax 6523, a crystalline isotactic polypropylene. The isotactic polymer shows a sharp yield at 20% elongation and essentially no recovery, giving a tensile set of 300%. ELPP has no yield and recovers over 200% from the original elongation, for a tensile set of 93%.

The elastic properties of ELPP and a blend of its fractions are further demonstrated by the hysteresis curves in Figure 5, which show partial elastic recovery as the sample is successively cycled to 300, 500, and 700% elongation, with a return to zero stress on each cycle.

Finally, Figure 6 compares the stress–strain curves for two samples of ELPP of different crystallinities with

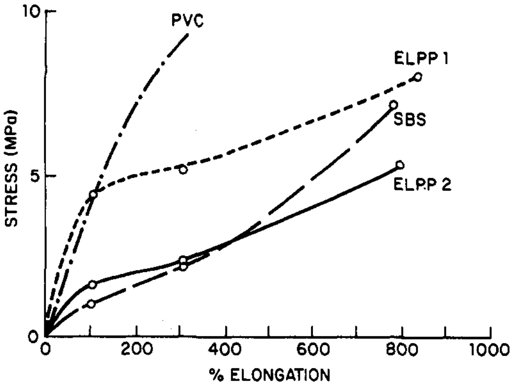

Figure 6. Stress–strain behavior of ELPP, PVC (Geon 8857), and SBS (Kraton 2705). The IR ratios of ELPP 1 and 2 were 0.53 and 0.23, respectively.

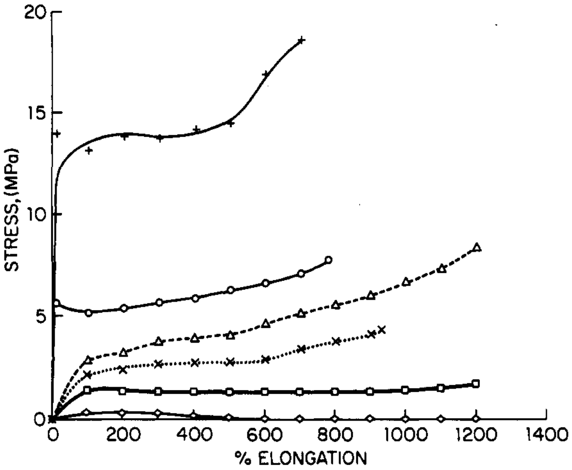

Figure 7. Stress–strain curves of ELPP and ELPP fractions at a strain rate of 20 in./min (51 cm/min): (△) whole polymer; (+) octane insoluble; (○) octane soluble; (×) heptane soluble; (□) hexane soluble; (◇) ether soluble.

Table IV
Multiple Solvent Fractionation of ELPP

solvent	wt fractn	η_{inh},[a] dL/g	crystallinity, %[b]
ethyl ether	0.36	0.66	0
hexane	0.11	1.79	14
heptane	0.14	1.98	24
octane	0.21	1.57	31
octane insol	0.17	6.69	69
whole polymer	1.00	2.92	31

[a] Inherent viscosity, 0.1 g/dL of solution in decalin at 135 °C. [b] Density crystallinity determined by displacement in methanol at 23 °C.

Kraton 2705, a hydrogenated styrene–butadiene–styrene thermoplastic elastomer, and with Geon 8857, a plasticized poly(vinyl chloride) (PVC). The curves show that the tensile properties of a thermoplastic elastomer or of a flexibilized plastic can be obtained by varying the isotacticity and molecular weight of polypropylene.

Properties of the Fractions. In order to determine the origin of the elastomeric properties, we have examined the properties of the diastereomeric fractions present. Typical data are in Tables III and IV.

The stress–strain curves of the fractions of Table IV are shown in Figure 7. The properties vary from a semicrystalline plastic (with a yield) for the most crystalline fraction, to a weak gum elastomer, for the ether–soluble fraction. The hexane- or heptane-soluble fraction is elastomeric and comparable to the elastomeric fractions reported by Natta et al.[1-3]

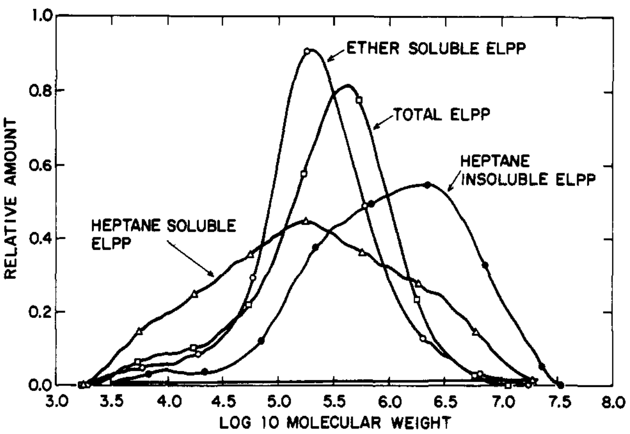

Figure 8. Molecular weight distribution of ELPP and fractions by gel permeation chromatography in 1,3,5-trichlorobenzene at 135 °C.

Table V
Cocrystallization by Melt Blending[a]

sample or blend	η_{inh},[e] dL/g	ether extract % sol.	ether extract η_{inh}	% extract insolubilized
a. ELPP, virgin	5.6	69	5.1	
b. ELPP, milled	5.3	37	1.8	47
c. blend of fractions[d]	5.0	36	1.7	48
d. c, precipitated	4.7	51	2.5	27
Profax–ether extract blends (1:1)				
e. ELPP extract[b]	nd	23	1.4	54
f. Afax extract[c]	nd	48	0.07	4

[a] Milled 10 min at 180 °C. [b] Ether soluble, η_{inh} = 4.40. [c] Ether soluble, η_{inh} = 0.21. [d] See text. Blend of ether soluble and ether insoluble. [e] nd, not determined.

Figure 8 shows molecular weight distributions of typical ELPP and its fractions. The molecular weights of ELPP fractions, in particular of the ether-soluble fractions, are significantly higher and broader than those of more stereoregular polypropylenes.

A key difference from earlier work of Natta[1-3] was the finding that the elastic properties of the polymer can be duplicated by combining the two extreme fractions; i.e., the elastic properties can be obtained without the central "elastic" fraction. This is demonstrated by the curves in Figure 5; the hysteresis for an ELPP polymer is essentially identical with the hysteresis of a blend of the ether-soluble and hexane-insoluble fractions isolated from the same polymer. Thus, ELPP is not merely a diluted elastomeric hexane-extractable fraction but possesses elastic properties throughout the polymer.

Cocrystallization and Elasticity. The elastomeric properties of the whole polymer appear to be the result of cocrystallization of the high molecular weight inherently elastomeric ether-soluble fraction with the more crystalline insoluble fractions. Boiling ether extraction studies showed that cocrystallization can be increased by melt blending.

Extraction of a virgin ELPP yielded 69% of an ether-soluble fraction with an inherent viscosity, η_{inh} = 5.1 (Table V, a). After the ELPP was milled for 10 min at 180 °C, only 36.5% was ether-soluble. Furthermore, the molecular weight of the extract decreased markedly to η_{inh} = 1.8, indicating that the high molecular weight species were not extracted (Table V, b). Essentially the same result was obtained if the ether-soluble and -insoluble fractions were recombined by milling, then extracted (Table V, c). The effect of cocrystallization could be partially reversed by dissolving the blend in decalin and precipitating prior to

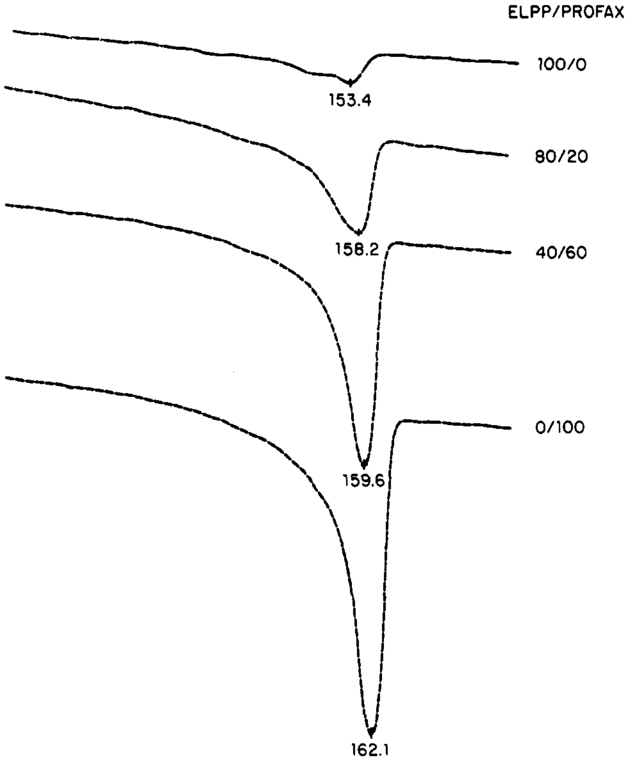

Figure 9. DSC heating curves of ELPP (η_{inh} = 2.2)/isotactic polypropylene (Profax 6723) blends. The peak melting temperature is in degrees Celsius.

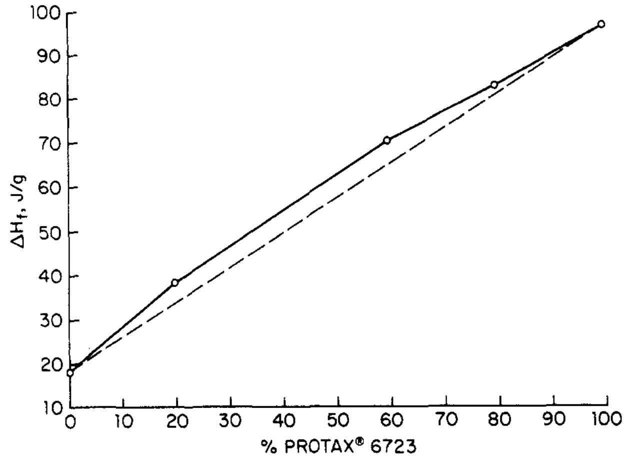

Figure 10. Heat of fusion versus percent Profax 6723 polypropylene melt blended with ELPP (η_{inh} = 2.2): (○) observed; (- - -) calculated, the sum of composition-weighted heats of fusion of the components.

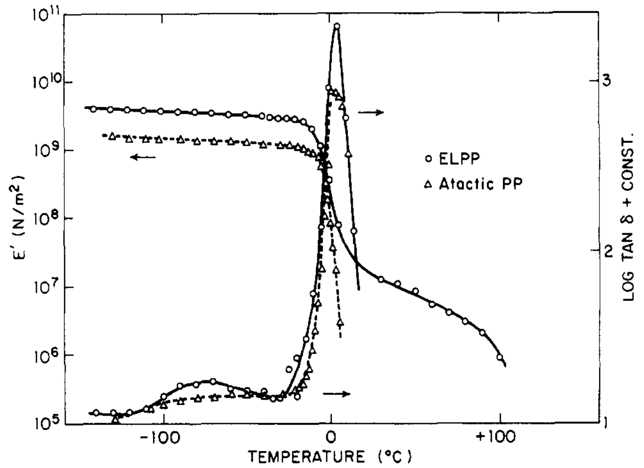

Figure 11. Dynamic mechanical spectroscopy of ELPP and atactic polypropylene (Afax). *E'* is the storage modulus and tan δ is the loss tangent.

ether extraction (Table V, d). However, the ether-soluble fraction was smaller and the molecular weight lower than for the virgin polymer.

Cocrystallization of the ether-soluble fraction of ELPP in a 1:1 melt blend with Hercules Profax polypropylene was also demonstrated (Table V, e). Only 46% of the original ether-soluble fraction was recovered and the η_{inh} was low, indicating selective retention of the high molecular weight species. In contrast, blending Profax 6523 with the ether-soluble fraction from Hercules Afax atactic polypropylene insolubilized only 4% of the added fraction (Table V, f). The low isotactic content of Afax (88% soluble in ether) and significantly lower molecular weight of the Afax extract (η_{inh} = 0.21 versus 4.4) inhibited retention by cocrystallization.

Further evidence for the cocrystallization was obtained by DSC of blends of ELPP with isotactic polypropylene (Figure 9). The DSC scans of the blends show substantial broadening of the melting range and lower melting points, the latter consistent with the formation of a homogeneous blend. A plot of the observed heat of fusion shows a positive deviation from the calculated value for all the blends (Figure 10), suggesting that some incipient crystallites in the ELPP are being incorporated into mixed crystals.

Dynamic mechanical spectra of ELPP and atactic polypropylene show a definite rubbery plateau in the 0–100 °C region only in the case of ELPP (Figure 11). This is also consistent with the presence of a network structure with strong cross-links.

The solvent fractionation, blending, extraction, and DSC results explain the difference between ELPP and stereoblock polypropylenes made with more stereospecific titanium chloride catalysts. In ELPP, the fractions can cocrystallize to form a homogeneous elastic network. With conventional Ti catalysts, the low molecular weight atactic fraction cannot cocrystallize with the highly isotactic fractions present and an incompatible blend results. More detailed analyses of the stereostructure, the crystallinity, and the morphology of ELPP and fractions are discussed in the accompanying paper.[32]

ELPP/Isotactic Polypropylene Blends. The compatibility of the high molecular weight low crystallinity polypropylenes with highly isotactic polypropylene permitted preparation and testing of blends. ELPP or the ether-soluble fraction may be used as the elastomeric material. Typical stress-strain properties for blends of Profax with an ether-soluble ELPP fraction are shown in Figure 12.

The elasticity of the blends was further evaluated by means of the tensile recovery test. Ether-soluble fractions with η_{inh} of <1 to >4 were tested alone and in 2:1 blends with a hexane-insoluble fraction (average blend isotacticity of 34%) and a 2:1 blend with Profax 6523 (average blend isotacticity 43%). Both the molecular weight of the ether-soluble fraction and the total isotacticity of the blend are important, as shown in Figure 13. The tensile set decreases (elastic recovery improves) as the molecular weight of the ether fraction increases or the total isotacticity decreases.

In blends of highly isotactic polypropylene and ether-soluble ELPP, a tensile set of >150% was usually associated with a plastic yield on the stress–strain curve. This was observed with ether fractions with η_{inh} less than about 2 (molec wt of 250 000). This yield may be the result of phase incompatibility of the two components and simulate

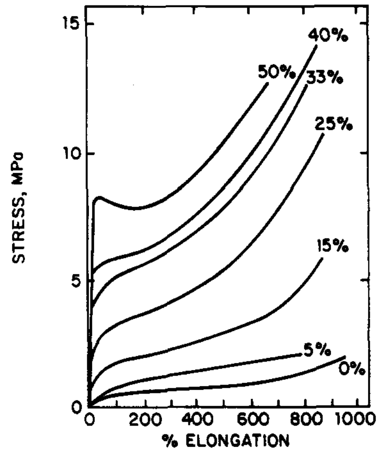

Figure 12. Stress–strain curves for blends of an ether-soluble ELPP fraction (η_{inh} = 4.4) with 0–50% Profax 6523 (isotactic) polypropylene.

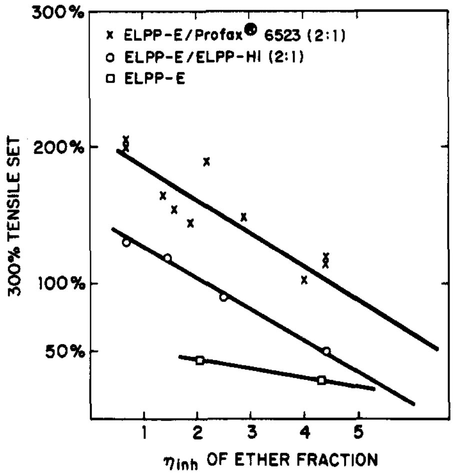

Figure 13. Tensile set as a function of molecular weight and isotacticity of ELPP fractions and blends. (×) Ether-soluble ELPP/Profax 6523 blend (2:1), ca. 43% isotactic; (○) ether-soluble/hexane-insoluble blend (2:1), ca. 39% isotactic; (□) ether-soluble ELPP, ca. 18% isotactic.

properties observed in many stereoblock polypropylenes made with $TiCl_4$ catalysts.

The high molecular weight ether-soluble fraction is the key component responsible for the elastic behavior. As a corollary, a good catalyst for the formation of elastomeric stereoblock polypropylenes must have low stereospecificity and produce high molecular weights. These criteria are not met by state-of-the-art high-activity titanium catalysts.

The blends based on the ether-soluble fractions can be considered a model of ELPP. The stress–strain curves show that products ranging of from soft elastomers to rigid plastics are attainable. Further, it is clear that the strength and stiffness are contributed by the crystalline component, while the elastic properties come from the amorphous component.

Stereoblock polypropylenes having elastomeric properties have also been prepared by alumina-supported bis(arene) Ti, Zr, and Hf catalysts.[53] Our work has also been extended to synthesis of elastomeric polybutenes.[54]

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Registry No. PP, 9003-07-0; i-PP, 25085-53-4; i-Bu_3Al, 100-99-2; i-BuAlH, 1191-15-7; $(PhCH_2)_4Ti$, 17520-19-3; $(PhC(CH_3)_2CH_2)_4Ti$, 60530-41-8; $(PhCH_2)_4Zr$, 24356-01-2; $(PhC(CH_3)_2CH_2)_4Zr$, 56797-10-5; $((CH_3)_3CCH_2)_4Zr$, 38010-72-9; $(PhC(CH_3)_2CH_2)_4Hf$, 84942-76-7; $ZrCl_4$, 10026-11-6; $Zr(BH_4)_4$, 12370-59-1.

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Elastomeric Polypropylenes from Alumina-Supported Tetraalkyl Group IVB Catalysts. 2. Chain Microstructure, Crystallinity, and Morphology

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ABSTRACT: Elastomeric polypropylene (ELPP)[1] and its components, separated by solvent extraction, have been characterized by NMR and IR spectroscopy, differential scanning calorimetry, size-exclusion chromatography, X-ray diffraction, nitric acid etching, and electron microscopy. The chain microstructure of ELPP is stereoblock, consisting of alternating isotactic and stereoirregular sequences, described approximately by second-order Markov polymerization statistics, which were used to calculate the distribution of isotactic block lengths. The results confirm that the high molecular weight ELPP fractions of low stereoregularity have isotactic blocks that cocrystallize with the more isotactic components to form an elastomeric network. The morphology consists of cocontinuous hard and soft phases, of crystalline isotactic and amorphous atactic polypropylene, respectively.

Background

In part 1, we reported the synthesis of a novel elastomeric polypropylene (ELPP) made by polymerizing propylene with highly active heterogeneous zirconium catalysts.[1] The elastic properties depend predominantly on the molecular weight of the ether-soluble ELPP fractions, while the strength and stiffness correlate with the total polymer crystallinity. According to our hypothesis, the isotactic segments of the ether-soluble ELPP cocrystallize with the larger isotactic blocks of the more stereoregular ELPP components, forming an elastic network.

In this paper, we explore further the origins of the elastomeric properties and structure–property relationships of ELPP by study of the chain microstructure, crystallinity, and morphology of components separated by solvent fractionation.

Experimental Section

Extraction. ELPP was separated by successive extraction of extruded blown film or extruded pellets with solvents of increasing boiling temperature, usually ether and hexane or heptane. Standard unjacketed Soxhlet extractors with 500-mL capacity tubes were used. The samples were blanketed with nitrogen during extraction. Extractions were continued until evaporation of the solvent showed that a negligible amount of polymer was extracted during a 24-h period, then extraction was continued with the next higher boiling solvent. The fractions were recovered by solvent evaporation.

NMR. Solutions of the polymers (10% w/v) were prepared in dideuteriotetrachloroethane or in 1:1 mixtures of $C_2D_2Cl_4$ with *o*-dichlorobenzene, containing 0.1% 2,6-di-*tert*-butyl-4-methylphenol (BHT) as a stabilizer. Proton-decoupled ^{13}C NMR spectra were measured with Bruker WH90 and WM400 spectrometers operating at 22.63 and 100.6 MHz, respectively, at sample temperatures of 120–145 °C. Differential saturation of the peaks was avoided by a 10-s delay between 90° pulses. The central peak of $C_2D_2Cl_4$ was taken as 74.14 ppm.

IR. A Nicolet FTIR spectrometer was used to obtain infrared spectra on melt-pressed films by transmission. The absorbances of the 997- and 993-cm^{-1} bands were used to calculate the IR ratio, A_{997}/A_{973}, a measure of the isotactic helix content.[2] Note that we employ the inverse of the ratio used by Luongo, because it correlates linearly with estimates of crystallinity by DSC, X-ray diffraction, and density measurements.

Test Specimens. All ELPP samples and fractions were compression molded by heating in a press under light pressure. The ether-soluble fractions were heated to 80 °C and all others to 180 °C for 10 min, then cooling water was run through the press platens, as full ram pressure of 276 MPa was applied and held until the platens were at room temperature.

DSC. Differential scanning calorimetry measurements of the test specimens were performed on a Du Pont 1090 thermal analyzer using a Du Pont 912 dual sample DSC module at a heating rate of 10 °C/min. The percent crystallinity, $100\Delta H_f/\Delta H_f°$, was calculated from the observed heat of fusion, ΔH_f, and $\Delta H_f° = 209$ J/g, the heat of fusion of crystalline polypropylene.[3]

X-ray. X-ray diffraction patterns of the specimens were obtained on a scanning diffractometer with Ni-filtered Cu Kα radiation. Crystallinity was calculated from the areas under the crystalline peaks versus the total scattering.

Density. Density crystallinity was measured by a buoyancy method with methanol as the buoyant medium. Five replicate measurements were made for each sample. The results were

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