Elastomeric Polypropylene Using Alumina-Supported Bis(Arene)Titanium and Tetra(Neophyl)Zirconium Catalysts

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ELASTOMERIC POLYPROPYLENE USING ALUMINA-SUPPORTED BIS(ARENE)TITANIUM AND TETRA(NEOPHYL)ZIRCONIUM CATALYSTS

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ABSTRACT

An overview of catalysts based upon tetra(neophyl)zirconium and bis(arene)titanium complexes supported on partially hydroxylated alumina for olefin polymerization is presented. The chemistry of the surface species has been partially elucidated. When these catalysts are used to polymerize propylene, the resulting stereoblock homopolymer is a thermoplastic elastomer. Physical and mechanical characterization of the polymer indicates that the properties may be attributed to an ether-soluble, largely amorphous, but high molecular weight fraction. The isotactic blocks in this largely atactic fraction cocrystallize with the crystalline, isotactic fraction to provide crosslinks in a rubbery network.

INTRODUCTION

Olefin polymerization using tetravalent, homoleptic complexes of titanium and zirconium supported on alumina as catalysts has received considerable attention [1]. Research at Du Pont has focused upon catalysts

based on tetra(neophyl)zirconium [2] and more recently bis(arene) complexes of titanium [1, 3] which only rarely have been reported [4]. In ethylene polymerization, these high activity catalysts retain activity at high temperatures; tetra(neophyl)zirconium-based catalysts function at temperatures as high as 300°C [5]. These temperatures allow higher production rates and economical recovery of the heat of polymerization. Like the MgCl$_2$-supported systems, a catalyst removal step is not required, and these catalysts have the additional advantage of imparting no chloride to the polymer.

In this paper we present an overview of the use of these catalysts in the polymerization of propylene. The products are elastomeric, stereoblock polymers which are composed of isotactic and stereoirregular sequences. Polymers made with catalysts based upon bis(mesitylene)titanium are stiffer than those derived from tetra(neophyl)zirconium-based catalysts. The chain microstructures of the various components of the whole polymers have been characterized by ^{13}C-NMR and solvent-extraction studies. The ether-soluble component of the polymers is of relatively high molecular weight and its backbone microstructure is largely stereoirregular, but there are isotactic segments. Cocrystallization of the short isotactic stereoblocks of the ether-soluble fraction with the crystalline, isotactic fractions is believed to be critical to the observed elastomeric properties.

CATALYST PREPARATION

Bis(mesitylene)titanium and other bis(arene)titanium compounds are readily prepared by cocondensation of titanium atoms onto a liquid-nitrogen-cooled surface with the appropriate arene using standard vapor-synthesis techniques [6]. They are dark purple compounds giving purple solutions in hydrocarbon solvents. Tetra(neophyl)zirconium (neophyl = $-CH_2CMe_2Ph$) and related compounds are readily prepared by reaction of the appropriate Grignard reagent with ZrCl$_4$. The results of an x-ray crystal structure determination shown in Fig. 1 indicate that tetra-(neophyl)zirconium has a diameter of about 12 Å.

The organometallics must be supported on high surface area alumina of controlled surface-hydroxyl content. Preparation of the alumina is critical and has been studied in some detail [7]. The most useful alumina is Degussa "C" fumed alumina which is made up of nonporous primary particles of 100–200 Å with an average pore diameter of 150–300 Å and a surface area of about 100 m²/g. The activity of the resulting catalyst is
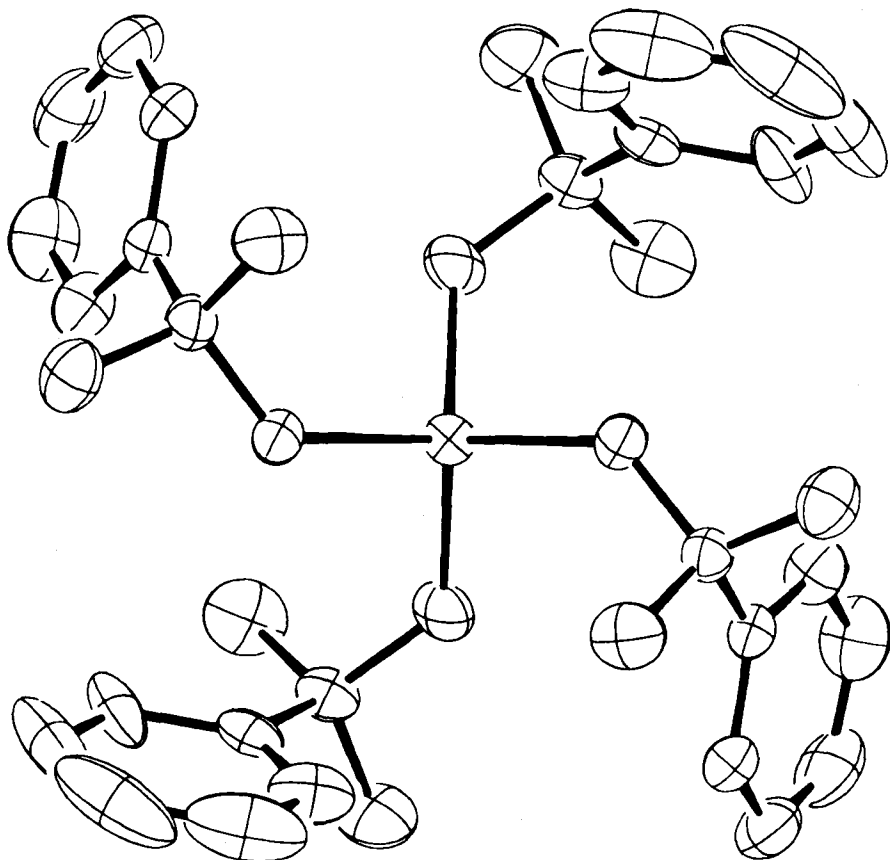
FIG. 1. Perspective view of tetra(neophyl)zirconium.

dependent on the drying conditions for the alumina and is at a maximum for a drying temperature of about 400°C. Titration of surface hydroxyls with MeMgBr yields 0.4–0.8 mmol/g or about one hydroxyl per 20–40 Å^2. When solutions of bis(arene)titanium complexes are reacted with the surface hydroxyls of the alumina, the characteristic purple color is discharged completely. Reaction with tetra(neophyl)zirconium causes no color change, but there is an immediate decrease in the viscosity of the alumina slurry.

Reaction of tetra(neophyl)zirconium with a small alumina column

provides information on the nature of the supported catalyst. The Zr—C bonds of tetra(neophyl)zirconium undergo protonolysis by the surface hydroxyls, liberating *tert*-butylbenzene with no change in the oxidation state of the metal. The supporting reaction is diffusion-controlled with the organometallics reacting first with the outermost hydroxyls [7]. On average, two neophyl groups are liberated in the initial reaction.
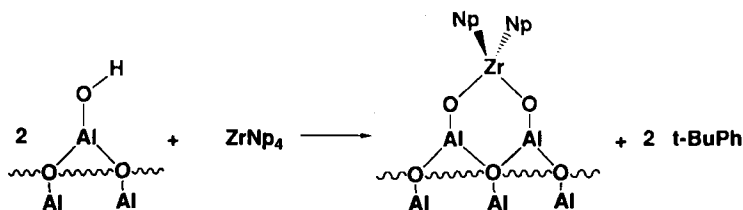

If the catalyst is exposed to hydrogen gas, an additional molecule of *tert*-butylbenzene is liberated and a broad band, observed at 1900 cm⁻¹ in the infrared spectrum, indicates the presence of a zirconium hydride. A schematic representation of the catalyst on a 100-Å alumina particle is presented in Fig. 2.

A similar reactivity pattern is not available in the zero-valent bis-(arene)titanium system. It is likely that there is an oxidative addition of a surface O—H bond to give at least a divalent supported species. The absence of color indicates oxidation to Ti(IV). Interestingly, only one coordinated arene is liberated during this reaction. The surface species remains coordinatively unsaturated — a feature required for an active polymerization catalyst.
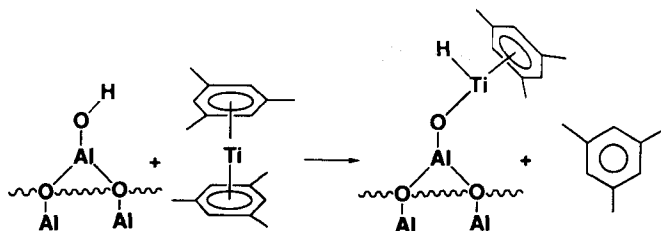
Insertion of olefin into the proposed metal hydride would initiate polymerization. An infrared study of the catalyst failed to detect the titanium

FIG. 2.   Representation of tetra(neophyl)zirconium supported on one of the primary particles of a partially hydroxylated alumina.
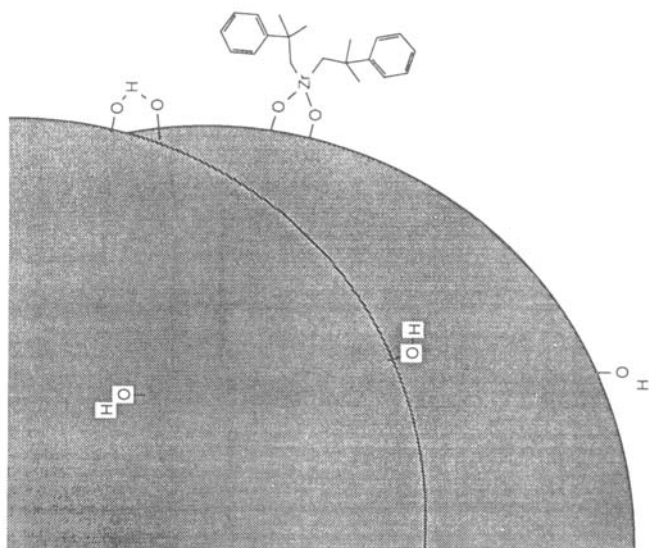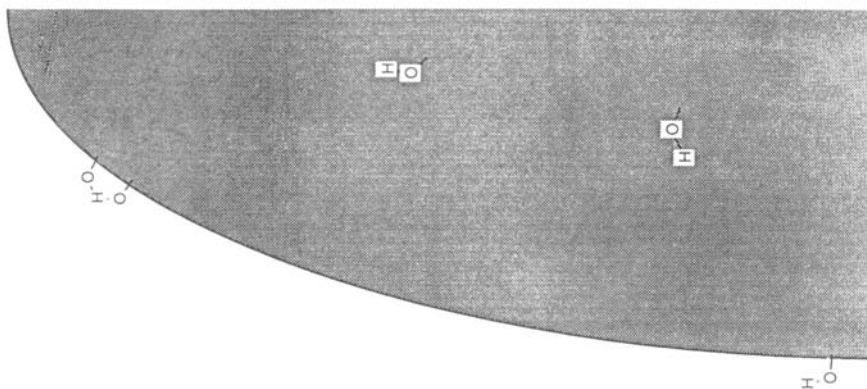
hydride stretching frequency, but a low conversion polymerization of ethylene on a surface-deuterated catalyst revealed deuterium incorporation into the terminal methyl group.

POLYMERIZATIONS

Polymerizations were carried out in a manner described earlier [1]. Initial experiments were designed to determine those factors which influenced the scope of the catalytic polymerization. Once the organometallic concentration is above the threshold for catalysts poisons in the system, there is a strong inverse correlation between the quantity of metal complex supported on the alumina and the productivity per supported complex. Metal loadings in the range of 0.1 to 0.2 mmol of metal per gram of alumina are most useful.

Temperature of polymerization influences the productivity of the catalyst. For ethylene polymerization, the bis(mesitylene)titanium-based catalysts are active from room temperature to 150°C, the highest temperature tested. The tetra(neophyl)zirconium-based catalysts function at temperatures as high as 300°C. At these temperatures, catalyst lifetimes are relatively short, but catalyst productivity is so high that there is no need to remove catalyst residues from the polymer. Exposure of the polymer to moisture converts the metal complexes to TiO_2 or ZrO_2. The polyethylene produced by both catalysts is of high density with a melting point of 137.5°C. Molecular weight can be controlled by the polymerization temperature or hydrogen. At lower temperatures in the absence of hydrogen, ultrahigh molecular weight polyethylene is obtained.

In contrast to the polyethylene polymerizations, productivity in propylene polymerizations goes through a maximum for both catalyst systems. The maximum productivity is generally found in the 60–80°C range and is dependent on the polymerization conditions. Again, the molecular weights are high, even when the polymerization is run in supercritical propylene.

The alumina-supported bis(mesitylene)titanium complexes become significantly more active in the presence of moderate amounts (25 psi partial pressure) of hydrogen. The hydrogen may be added during the polymerization, but the addition is most effective if carried out after supporting the catalyst but before the polymerization is initiated. At this time we have little insight into the changes taking place in the catalyst. Response of the tetra(neophyl)zirconium supported on alumina is the

same; as noted above, an additional molecule of *tert*-butylbenzene is liberated upon the hydrogen treatment, leaving at most one alkyl group bonded to the metal center. The increased reactivity with hydrogen indicates that a new surface species has been produced, though it is not clear whether the increased activity results from more active sites or higher productivity for the existing sites.

Polymerization of propylene with prehydrogenated bis(mesitylene)titanium catalysts in the presence of low pressures of hydrogen does not noticeably lower the polymer molecular weight as indicated by inherent viscosities of as high as 20 dL/g. This is in contrast to catalysts derived from tetravalent metals [tetra(benzyl)titanium or tetra(neophyl)zirconium] supported on alumina where pressures of 40 psi hydrogen lowered the inherent viscosity values of the polymers to 5–7.5 from values of 16–20 dL/g. Significant inherent viscosity lowering is obtained with the bis-(mesitylene)titanium-based catalysts by carrying out propylene polymerizations in the presence of very high hydrogen partial pressures (e.g., 200–500 psi). Under these conditions, polypropylenes with inherent viscosities of 7.4–12.0 dL/g are obtained in good conversions.

The polypropylene molecular weight is lowered significantly by treating the supported bis(mesitylene)titanium catalyst with a small amount of aluminum alkyl prior to polymerizations in the presence of 80 psi of hydrogen. With catalyst ratios AlR_3 : Ti of 0.65 to 0.89, there is a moderate lowering in inherent viscosity with little loss in productivity. With a R_3Al : Ti ratio of 1.1, a polymer with an inherent viscosity of 6.4 dL/g is produced, but with significant loss in productivity. Diethylzinc also lowers the molecular weight, but higher ratios of metal to titanium are required.

In polymerizations with $MgCl_2$-supported $TiCl_4$ catalysts, the addition of Lewis base electron-donors can increase stereoregularity significantly [8]. This is usually at the expense of productivity, but in some catalysts exhibiting nonclassical behavior, stereoregularity and productivity can be increased simultaneously [9]. In the catalyst systems reported here, addition of ethyl benzoate poisons the catalysts with little effect on the polymer obtained. Only 0.04–0.06 molar equivalents are required to totally poison the tetra(neophyl)zirconium-based catalysts, putting an upper limit on the number of active sites. In the case of the bis(mesitylene)titanium catalysts, 0.6 molar equivalents of ethyl benzoate are required; this may indicate that 60% of the titanium sites are catalytically active or it may indicate less selectivity in the reaction of ethyl benzoate with active sites.

MECHANICAL CHARACTERIZATION OF ELASTOMERIC POLYPROPYLENE

The polypropylenes produced by both the tetra(neophyl)zirconium and bis(arene)titanium catalysts are elastomeric. The properties of elastomeric polypropylenes (ELPP) produced with catalysts based upon tetra-(neophyl)zirconium have been reported [10]. The fractionation studies discussed below indicate that the polymers obtained with both catalyst systems are made up of a range of components which are presumably produced at different types of active sites. The key component of these polymers is a high molecular weight ether-soluble fraction which cocrystallizes with the crystalline fraction to form a thermoplastically cross-linked network [11].

Unlike isotactic polypropylene, test bars of ELPP show no yield point when extended in stress-strain measurements. Typical curves are shown in Fig. 3. The elongated polymers show the hysteresis curves typical of elastic recovery. The values of the tensile set after 300% elongation for bis(arene)titanium-derived ELPP range from 90 to 150%, which is greater than the range of 60 to 130% for polymers derived from tetra(neo-phyl)zirconium. It is interesting to note that these polymers are stiffer than the tetra(neophyl)zirconium-derived polymers; forces of 550 to 725 N/cm² are required to achieve 100% elongation (M_{100}), while the tetra-(neophyl)zirconium-derived polymers typically require less than 550 N/cm². This higher stiffness is a result of a higher degree of crystallinity or
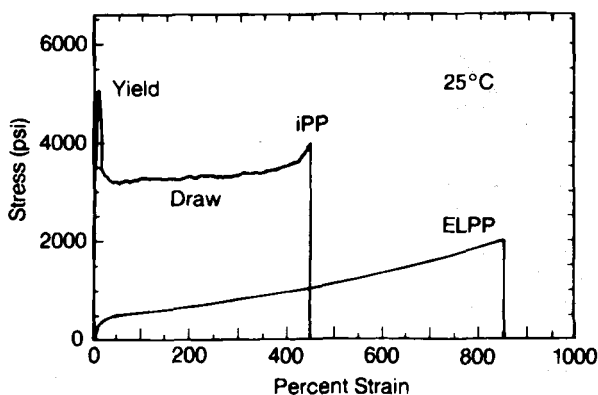

FIG. 3.   Stress-strain curves of isotactic and elastomeric polypropylene.

crystalline content. The infrared crystallinity index of the whole polymers is generally 0.50 to 0.60, while the tetra(neophyl)zirconium-derived polymers generally have crystallinity indices below 0.50. The higher stiffness of the bis(arene)titanium-derived ELPP is also indicated in the breaking points of the polymers. Behavior on stretching to the break point is that of a typical elastomer in that no yield point is observed. Observed values of stress-at-break of up to 1300 N/cm² may be compared to those of the tetra(neophyl)zirconium-derived polymers which rarely exceeded 1000 N/cm². Elongations at break average 600% while the zirconium-derived polymers average over 800%.

The area under a stress-strain curve integrated to break is an indication of the "toughness" of the polymer. While the bis(arene)titanium-derived polymers generally break at shorter elongations, the higher values of tension give an integrated toughness greater than those observed for the tetra(neophyl)zirconium-based polymers. Maximum toughness occurs in bimodal networks where short chains improved ultimate strength and long chains give extensibility [12].

The marked temperature dependence of the toughness of ELPP is indicated in Fig. 4. Elongation goes through a maximum close to room temperature. As temperature is lowered, toughness is maintained by the increasing stress. As temperature is increased, both elongation and stress fall off, causing a dramatic decrease in toughness.

FRACTIONATION AND NMR CHARACTERIZATION

ELPP is readily fractionated by extraction with diethyl-ether, hexane, and heptane. Regio- and pentad stereoregularities of typical whole polymers and their solvent fractions can be determined by ¹³C NMR; typical spectra are shown in Fig. 5. The solvent fractionation is on the basis of structure or crystallinity as well as molecular weight. In the titanium-derived polymers, the ether-soluble fraction is normally in the 20-40% range of the total polymer with an average of 30%. In general, the molecular weights of polymers obtained from the zirconium catalysts under similar polymerization conditions are lower. This same observation holds for the ether-soluble fractions of the two classes of polymers. While the ether-soluble fraction has the lowest molecular weight and the insoluble fraction the highest, the molecular weight distributions for all the various fractions are relatively broad and overlapping. The weight fraction of
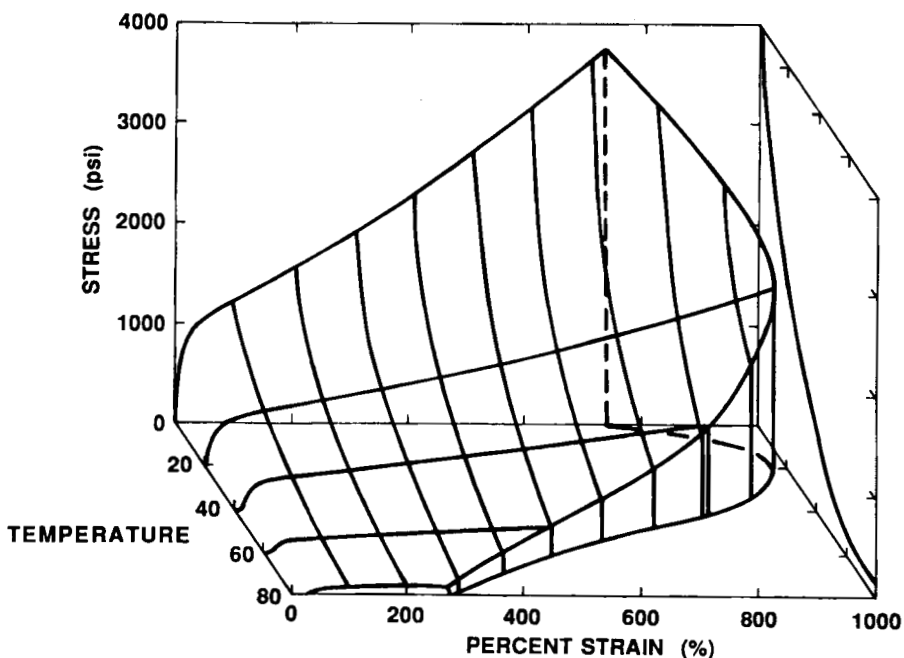
FIG. 4. Stress-strain behavior of elastomeric polypropylene as a function of temperature.

crystalline polymer increases from the ether-soluble fraction to the insoluble fraction.

NMR analysis of regioregularity and stereoregularity of the fractions reveals that the observed crystallinity correlates with the chain microstructure. The number of monomer reversals decreases and the isotactic block-length becomes longer in going from the ether-soluble to the heptane-insoluble fractions of the polymer. For one bis(arene)titanium-based polymer, the ratio of the relative areas of the mmmm and mmmr pentad peaks indicates that the probability, $P(mm/m)$, that a growing polymer chain will add the next monomer unit to form an mmm sequence is 0.74. For a single polymer chain with $P(mm/m) = 0.74$ to have two or more isotactic sequences of 16 or more units, the molecular weight would have to be in excess of 200,000. It is clear that an appreciable percent of the ether-soluble fraction meets this criterion. The heptane-soluble fraction, with $P(mm/m) = 0.86$, would have an appreciable number of isotactic
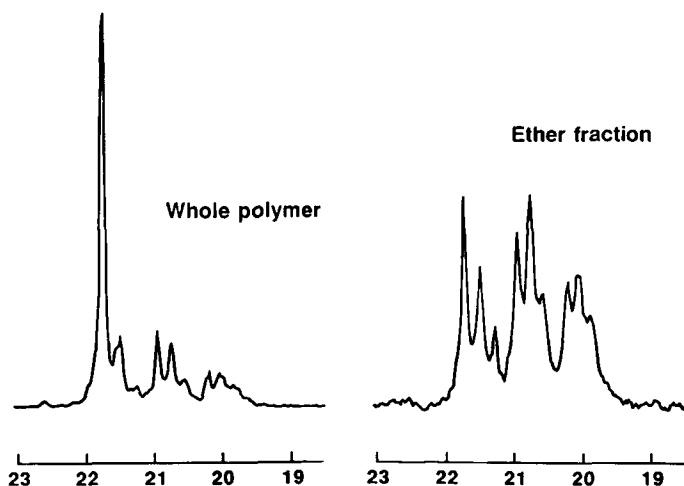
Fig. 5. ^{13}C-NMR spectra of whole ELPP and the ether-soluble fraction.

blocks of 16 or more units per polymer chain, yet the fraction retains an appreciable atactic component.

Isotactic blocks with a minimum of 12 to 16 units are able to cocrystal-lize with the isotactic fractions of the polymer, though isotactic blocks as short as 9 units having three turns of the polypropylene helix could show appreciable interaction with isotactic crystallites. Cocrystallization of the smaller blocks is very dependent on the rate of crystallization, with the shorter segments being excluded when crystallization takes place more slowly. Because of the appreciable atactic chain length between the blocks, the isotactic blocks in a single polymer chain do not necessarily cocrystallize in the same crystallite. Thus the atactic segments serve as amorphous, flexible links between adjacent crystalline regions. Schemat-ic representations of isotactic and elastomeric polypropylenes are shown in Fig. 6. While the bis(arene)titanium-derived polymers contain less of the ether-soluble fraction than the tetra(neophyl)zirconium-derived poly-mers, the longer chain length increases the likelihood that the isotactic blocks of a given polymer chain can cocrystallize in several different crystallites. This greater number of flexible, amorphous links between the crystallites accounts for the enhanced toughness observed in these polymers.
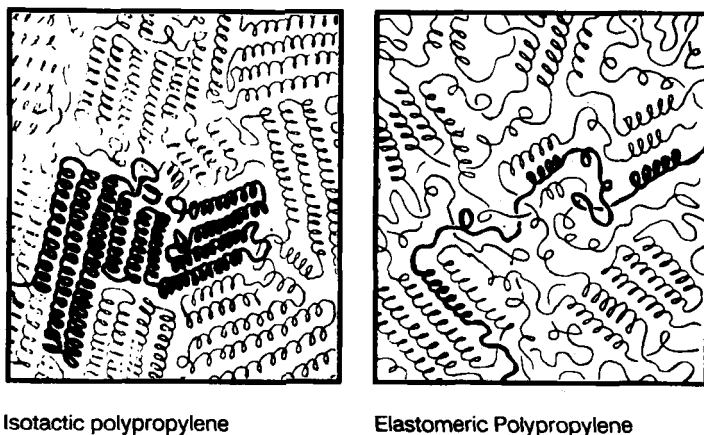
Isotactic polypropylene   Elastomeric Polypropylene

FIG. 6.   Schematic representations of isotactic and elastomeric polypropy-
lene highlighting the course of one polymer chain.

CONCLUSIONS

There are a wide variety of surface hydroxyls and environments on
partially hydroxylated alumina. When organometallics are supported on
the alumina, reactions with these hydroxyls lead to a range of catalytical-
ly-active sites. The stereochemical microstructure of the individual poly-
mer chains coming from these diverse sites varies dramatically, ranging
from isotactic to stereoblock to atactic. The one common feature of the
range of polymer chains is their high molecular weight. These features
differentiate ELPP from Natta's early unselective catalysts in that his
polymers consisted of lower molecular weight atactic polymer and higher
molecular weight isotactic polymer coming from two different classes of
sites. Early polypropylene plants had to invest considerable energy into
the separation and disposal of the large atactic fraction.

The high molecular weight, ether-soluble fraction of the polymer is the
key to the observed elastomeric behavior. The molecular weights of both
the ether-soluble and the heptane-insoluble fractions of polymers are
increased on going from the tetra(neophyl)zirconium-based to the bis-
(arene)titanium-based catalysts. The increase in the molecular weight of
the atactic polymer fraction allows cocrystallization with a greater frac-
tion of the isotactic components. As a result, the toughness of the poly-
mer increases substantially with only moderate degradation of the elasto-
meric properties.

More detailed investigations of the ELPP system will be reported in the future. These will include the effects of catalysts and polymerization conditions on the ELPP's produced; the nature of ELPP, its various fractions, and how they interact to affect polymer properties; and the thermal and mechanical properties of ELPP.

ACKNOWLEDGMENTS

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