NEW DIBLOCK COPOLYMERS CONSISTING OF POLYOLEFIN AND FUNCTIONAL POLYMER SEGMENTS

Diblock copolymers comprising a polyolefin segment and a functional polymer segment and having the structural formula: (Polyolefin Segment)-f-(Functional Polymer Segment), wherein f is a chemical linkage, such as an ether, ester or amid group linkage, have been prepared by contacting a polyolefin having a terminal borane group with a free radical polymerizable monomer or by reacting a functionalized polyolefin with a cyclic monomer capable of undergoing ring opening polymerization using the functional group on the functionalized polyolefin as the initiator for the ring opening polymerization. The diblock copolymers are useful as interfacial materials for improving the interaction between polyolefins and other materials.
<table>
<thead>
<tr>
<th>Code</th>
<th>Country</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>Albania</td>
</tr>
<tr>
<td>AM</td>
<td>Armenia</td>
</tr>
<tr>
<td>AT</td>
<td>Austria</td>
</tr>
<tr>
<td>AU</td>
<td>Australia</td>
</tr>
<tr>
<td>AZ</td>
<td>Azerbaijan</td>
</tr>
<tr>
<td>BA</td>
<td>Bosnia and Herzegovina</td>
</tr>
<tr>
<td>BB</td>
<td>Barbados</td>
</tr>
<tr>
<td>BE</td>
<td>Belgium</td>
</tr>
<tr>
<td>BF</td>
<td>Burkina Faso</td>
</tr>
<tr>
<td>BG</td>
<td>Bulgaria</td>
</tr>
<tr>
<td>BJ</td>
<td>Benin</td>
</tr>
<tr>
<td>BR</td>
<td>Brazil</td>
</tr>
<tr>
<td>BY</td>
<td>Belarus</td>
</tr>
<tr>
<td>CA</td>
<td>Canada</td>
</tr>
<tr>
<td>CF</td>
<td>Central African Republic</td>
</tr>
<tr>
<td>CG</td>
<td>Congo</td>
</tr>
<tr>
<td>CH</td>
<td>Switzerland</td>
</tr>
<tr>
<td>CI</td>
<td>Côte d'Ivoire</td>
</tr>
<tr>
<td>CM</td>
<td>Cameroon</td>
</tr>
<tr>
<td>CN</td>
<td>China</td>
</tr>
<tr>
<td>CU</td>
<td>Cuba</td>
</tr>
<tr>
<td>CZ</td>
<td>Czech Republic</td>
</tr>
<tr>
<td>DE</td>
<td>Germany</td>
</tr>
<tr>
<td>DK</td>
<td>Denmark</td>
</tr>
<tr>
<td>EE</td>
<td>Estonia</td>
</tr>
<tr>
<td>ES</td>
<td>Spain</td>
</tr>
<tr>
<td>FI</td>
<td>Finland</td>
</tr>
<tr>
<td>FR</td>
<td>France</td>
</tr>
<tr>
<td>GA</td>
<td>Gabon</td>
</tr>
<tr>
<td>GB</td>
<td>United Kingdom</td>
</tr>
<tr>
<td>GE</td>
<td>Georgia</td>
</tr>
<tr>
<td>GH</td>
<td>Ghana</td>
</tr>
<tr>
<td>GN</td>
<td>Guinea</td>
</tr>
<tr>
<td>GR</td>
<td>Greece</td>
</tr>
<tr>
<td>HU</td>
<td>Hungary</td>
</tr>
<tr>
<td>IE</td>
<td>Ireland</td>
</tr>
<tr>
<td>IL</td>
<td>Israel</td>
</tr>
<tr>
<td>IS</td>
<td>Iceland</td>
</tr>
<tr>
<td>IT</td>
<td>Italy</td>
</tr>
<tr>
<td>JP</td>
<td>Japan</td>
</tr>
<tr>
<td>KE</td>
<td>Kenya</td>
</tr>
<tr>
<td>KG</td>
<td>Kyrgyzstan</td>
</tr>
<tr>
<td>KP</td>
<td>Democratic People's</td>
</tr>
<tr>
<td>KR</td>
<td>Republic of Korea</td>
</tr>
<tr>
<td>KZ</td>
<td>Kazakhstan</td>
</tr>
<tr>
<td>LC</td>
<td>Saint Lucia</td>
</tr>
<tr>
<td>LI</td>
<td>Liechtenstein</td>
</tr>
<tr>
<td>LK</td>
<td>Sri Lanka</td>
</tr>
<tr>
<td>LR</td>
<td>Liberia</td>
</tr>
<tr>
<td>LS</td>
<td>Lesotho</td>
</tr>
<tr>
<td>LT</td>
<td>Lithuania</td>
</tr>
<tr>
<td>LU</td>
<td>Luxembourg</td>
</tr>
<tr>
<td>LV</td>
<td>Latvia</td>
</tr>
<tr>
<td>MC</td>
<td>Monaco</td>
</tr>
<tr>
<td>MD</td>
<td>Republic of Moldova</td>
</tr>
<tr>
<td>MG</td>
<td>Madagascar</td>
</tr>
<tr>
<td>MK</td>
<td>The former Yugoslav</td>
</tr>
<tr>
<td>ML</td>
<td>Mali</td>
</tr>
<tr>
<td>MN</td>
<td>Mongolia</td>
</tr>
<tr>
<td>MR</td>
<td>Mauritania</td>
</tr>
<tr>
<td>MW</td>
<td>Malawi</td>
</tr>
<tr>
<td>MX</td>
<td>Mexico</td>
</tr>
<tr>
<td>NE</td>
<td>Niger</td>
</tr>
<tr>
<td>NL</td>
<td>Netherlands</td>
</tr>
<tr>
<td>NO</td>
<td>Norway</td>
</tr>
<tr>
<td>NZ</td>
<td>New Zealand</td>
</tr>
<tr>
<td>PL</td>
<td>Poland</td>
</tr>
<tr>
<td>PT</td>
<td>Portugal</td>
</tr>
<tr>
<td>RO</td>
<td>Romania</td>
</tr>
<tr>
<td>RU</td>
<td>Russian Federation</td>
</tr>
<tr>
<td>SD</td>
<td>Sudan</td>
</tr>
<tr>
<td>SE</td>
<td>Sweden</td>
</tr>
<tr>
<td>SG</td>
<td>Singapore</td>
</tr>
<tr>
<td>SI</td>
<td>Slovenia</td>
</tr>
<tr>
<td>SK</td>
<td>Slovakia</td>
</tr>
<tr>
<td>SN</td>
<td>Senegal</td>
</tr>
<tr>
<td>SZ</td>
<td>Swaziland</td>
</tr>
<tr>
<td>TD</td>
<td>Chad</td>
</tr>
<tr>
<td>TG</td>
<td>Togo</td>
</tr>
<tr>
<td>TJ</td>
<td>Tajikistan</td>
</tr>
<tr>
<td>TM</td>
<td>Turkmenistan</td>
</tr>
<tr>
<td>TR</td>
<td>Turkey</td>
</tr>
<tr>
<td>TT</td>
<td>Trinidad and Tobago</td>
</tr>
<tr>
<td>UA</td>
<td>Ukraine</td>
</tr>
<tr>
<td>UG</td>
<td>Uganda</td>
</tr>
<tr>
<td>US</td>
<td>United States of America</td>
</tr>
<tr>
<td>UZ</td>
<td>Uzbekistan</td>
</tr>
<tr>
<td>VN</td>
<td>Viet Nam</td>
</tr>
<tr>
<td>YU</td>
<td>Yugoslavia</td>
</tr>
<tr>
<td>ZW</td>
<td>Zimbabwe</td>
</tr>
</tbody>
</table>
New Diblock Copolymers Consisting of Polyolefin and Functional Polymer Segments

Field of the Invention

This invention relates to block copolymer and, more particularly, to diblock copolymers consisting of polyolefin and functional polymer segments which are chemically bonded to each other at their respective chain ends by means of a functional group linkage, such as an ether, ester or amide functional group linkage. The chemistry that is used to prepare the diblock copolymers is based on the use of a polyolefin that is terminated with a functional group, such as -BR₁R₂, -OH, -NH₂ or a halide. Under certain reaction conditions, the functional group serves as the initiator for free radical polymerization of free radical polymerizable monomers, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA) and styrene or as the initiator for ring-opening polymerization of cyclic functional monomers, such as lactones, lactams, cyclic ethers and 2-oxazolines.

The invention also relates to a process for preparing such diblock copolymers. The diblock copolymers are useful as interfacial materials for improving the interaction between polyolefins and other materials.

Background of the Invention

Although useful in many commercial applications, polyolefins suffer a
major deficiency, i.e., poor interaction with other materials. The inert nature of polyolefins significantly limits their end uses, particularly those in which adhesion, dyeability, paintability, printability or compatibility with other functional polymers is paramount. The poor compatibility of polyolefins is evidenced, for example, by a weak adhesion between polyolefins and metal surfaces such that polyolefins have not been used effectively as a protective coating for metals. Furthermore, attempts to blend polyolefins with other polymers have been unsuccessful for much the same reasons, i.e., the incompatibility of the polyolefins and the other polymers.

In general, polyolefins have been among the most difficult materials to chemically modify both by functionalization reactions and by graft reactions. In post-polymerization reactions, the inert nature and crystallinity of polyolefins usually dictates the need for rather severe reaction conditions to effect any chemical modification. In many cases, the necessary reaction conditions result in serious side reactions, such as degradation in case of polypropylene modification reactions. In the direct polymerization of olefins, the only commercially viable processes for preparing linear polyolefins are those which utilize Ziegler-Natta catalysis. However, it is generally difficult to incorporate functional group-containing monomers into a linear olefin polymer that is prepared by means of a Ziegler-Natta polymerization due to catalyst poisons, see J. Boor, Jr., Ziegler-Natta Catalysts and Polymerizations; Academic Press: New York,(1979). It is clear that there is a fundamental need to develop a new chemistry which can address the challenge of preparing both functionalized and block/graft copolymers of polyolefins in a controllable fashion.
U.S. Patents 4,734,472, 4,751,276, 4,812,529 and 4,877,846, relate to borane-containing polyolefins. The chemistry disclosed in those patents involves the direct polymerization of organoborane-substituted monomers and α-olefins in Ziegler-Natta processes to form homopolymers and copolymers which contain borane groups and which are useful intermediates for preparing a series of functionalized polyolefins.

Chinsipikul et al., J. Thermoplastic Composite Materials 6, 18-28, (1993) demonstrates that the addition of polar groups to polyolefins can improve the adhesion of polyolefins to many substrates, such as metals and glass.

U. S. Patent 5,286,800 has extended the chemistry of borane containing polymers to the preparation of polyolefin graft copolymers by means of a free radical graft-from reaction.

Chung et al., Macromolecules 26, 3467-3471, (1993) and Chung et al., Macromolecules, 27, 1313-1319, (1994) disclose that the incompatibility of polymers in a blend can be improved by adding a suitable polyolefin graft copolymer which reduces the domain sizes of the respective polymers in the blend and increases the interaction between domains.

which alters the morphology of the blends as well as interfacial adhesion between domains.

In the past, most diblock copolymers have been produced by sequential anionic living polymerization processes (U. S. Patent 3,265,765), by sequential cationic living polymerization processes (U. S. Patent, 4,946,899), and more recently by metathesis living polymerizations (Cannizzo, et al. Macromolecules 21, 1961-1967, (1988)). However, living polymerization processes are limited by the relatively small number of monomers which undergo living propagation, and by the difficulties in the crossover reaction from one monomer to the other.

The extension of sequential living polymerization to Ziegler-Natta polymerization, for the preparation of polyolefin diblock copolymers, has been very limited. Only a few such preparation have been reported (Doi, et al., Makromol. Chem. 186, 11-15,(1985), Doi et al., Adv. Polym Sci., 73/74, 201-248, (1989) and H. Yasuda, et al., Macromolecules, 25, 5115-5116 (1992), and those involved the use of very inconvenient reaction conditions and special catalysts.

homopolymers and perhaps some block copolymer. Based on measured lifetimes of the growing chains and efficiency of the coupling reaction, the yields of polyolefin diblock copolymers are well below 20%.

Summary of the Invention

It is an object of the present invention to provide diblock copolymers consisting of polyolefin segments bonded through functional group linkages to functional polymer segments.

It is another object to provide a process for preparing polyolefin diblock copolymers, which process is capable of achieving a high yield (> 80%) and a controllable composition.

These and other objects and advantages of the invention are achieved by utilizing a transformation reaction from transition metal coordination (Ziegler-Natta and metallocene) to free radical and ring-opening polymerizations. Both polymerization processes offer good control in polymer molecular weight and the transformation reaction is very effective under mild reaction conditions. The resulting new class of polyolefin diblock copolymers consist of a polyolefin polymer segment and a functional polymer segment which are chemically bonded at the respective chain ends via a functional group linkage.

The diblock copolymers of the present invention may be characterized as follows:

(polyolefin segment)-f-(functional polymer segment)

wherein f is a chemical linkage, such as an ether, ester or amide group linkage. The
polyolefin segment is a homo- or co-polymer prepared by transition metal coordination polymerization of at least one C₂ - C₁₂ α-olefin, such as ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, styrene and mixtures thereof.

The molecular weight of the polyolefin segment is above about 2,000 g/mole.

Preferably the molecular weight range of the polyolefin segment is from about 10,000 to about 1,000,000 g/mole, and more preferably from about 10,000 to about 200,000 g/mole. The polyolefin segment may comprise an isotactic, syndiotactic or atactic structure. The functional polymer segment, chemically bonded to the polyolefin segment, is a polymer which is prepared either by free radical polymerization of a free radical polymerizable monomer, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA) and styrene, or by ring-opening polymerization of a cyclic functional monomer, such as a lactone, lactam, 2-oxazoline or cyclic ether. The molecular weight of the functional polymer segment is above about 500 g/mole, preferably from about 2,000 to about 1,000,000 g/mole, and more preferably from about 10,000 to about 200,000 g/mole. The functional polymer segment may comprise from about 1 to about 95 wt.% of the diblock copolymer. Typically, the functional polymer segment will comprise from about 5 to about 80 wt.% of the diblock copolymer.

In one aspect of the invention, the preparation of diblock copolymers is based in part on the use of chain-end unsaturated polyolefins which are prepared by transition metal (Ziegler-Natta) catalysts. By using borane chemistry, the chain-end unsaturated polyolefins are effectively functionalized to telechelic polyolefins.
which have a functional group located at the chain end. Suitable functional groups include, for example, -OH, -NH₂, -CHO, a halide, or -BR₁R₂, where R₁ and R₂ can be the same or different and are H, a halide, a C₁ to C₅ alkoxide or a C₁ to C₂₀ linear or branched alkyl or cyclic or bicyclic structure.

Under reaction conditions disclosed herein, the functional group at the chain end is then used as the catalytic site for either free radical polymerization of a free radical polymerizable monomer, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA) and styrene, or for ring-opening polymerization and copolymerization of cyclic functional monomers, such as lactones, lactams, 2-oxazolines and cyclic ethers. The free radical and ring-opening polymerized polymers are chemically bonded to the chain end of a polyolefin. By this synthetic route, high block efficiency is observed with very low concentration of homopolymer. In addition, the desired molecular structure and composition of the diblock copolymer can be obtained.

In another aspect of the invention, the chain-end functional group is used as the reactive site for transesterification reactions. By mixing the chain end functional polymer with a preformed polyester polymer, a diblock copolymer structure can also be obtained, e.g. polyolefin-f-polyester, wherein f is a chemical linkage. In fact, the transesterification reaction may take place simultaneously with a ring opening polymerization of a cyclic ester, thus resulting in the formation of a mixture of copolymers, e.g., a mixture of polyolefin-f-polyester and polyolefin segment -f-functional polymer segment.

The polyolefin diblock copolymers of the invention are extremely useful
in their own right, i.e., when they are used by themselves. For example, the present
diblock copolymers may be used as water-wettable polyolefins, molding
compositions, or the like. However, the present diblock copolymers are
particularly useful as interface modifiers, such as compatibilizers in polyolefin
blends and composites. When used in such blends, the diblock copolymers serve
as an emulsifier to alter the morphology of the blends. More particularly, the
diblock copolymers reduce the domain sizes for the polymers of the blend and
increase the interaction at the interface between the various domains. In polyolefin
coating applications, this invention also provides a method for producing
polyolefin/substrate laminate products, such as polypropylene/aluminum and
polypropylene/glass, which are characterized by good adhesion at the
polyolefin/substrate interface. The polyolefin diblock copolymer locates at the
interface and provides the interface adhesion between polyolefin film and substrate.

Detailed Description of the Invention

The present invention is based upon a specific class of diblock copolymers
which have wide range of properties, including an ability for improving interface
interactions between polyolefins and other materials. Most particularly, these
diblock copolymers can be formed with high efficiency and desirable molecular
microstructures, which include covalent bonds between two polymer segments. The
diblock copolymers are soluble in organic solvents and for this reason the diblock
copolymers are suitable for a variety of applications. For example, by using these
diblock copolymers as compatibilizers, it has been found that they can serve as
emulsifiers at the interface between two polymer domains so as to greatly change the morphology of these blends. One benefit of this change in morphology is that the macro phase separation between two incompatible polymers is altered and the phase size can be dramatically reduced, there by enabling domain sizes as small as about 10 nm to be achieved.

The chemistry to prepare the diblock copolymers of the invention is based on the use of intermediate polyolefins (II) and (III), as shown in following equation, which intermediate polyolefins have been obtained by functionalization of the chain-end unsaturated polyolefin (I) using borane chemistry.

In the above equation, F is a polar functional group, such as -OH, -NH₂, -halide or -CHO; R and R' can be the same or different and are a proton (H), a halide, or a C₁-C₂₀ alkyl, phenyl or alkyl-substituted phenyl group; and R₁ and R₂ can be the
same or different and are a proton (H), or a linear or branched alkyl group, or a cyclic or bicyclic structure. Representative examples of \( R \) and \( R' \) include, but are not limited to proton, methyl, ethyl propyl, butyl, iso-butyl, hexyl, octyl, decyl, phenyl, p-tolyl and o-tolyl groups. Similarly, representative examples of \( R_1 \) and \( R_2 \) include proton, chloro, bromo, iodo, methyl, ethyl, n-butyl, sec-butyl, iso-butyl, iso-amyl, 2, 3-dimethyl-2-butyl, n-pentyl, iso-pentyl, n-hexyl, neopentyl, phenyl, benzyl, cyclopentyl, cyclohexyl, diisopinocampheyl, 9-borodicyclo[3,3,1] nonane, 3, 5 dimethylborinane, boracyclopentane, boracyclohexane and boracycloheptane.

The polyolefin segment is a homo- or copolymer prepared by transition metal coordination polymerization of \( \alpha \)-olefins, such as ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, styrene and their mixtures. The polyolefin segment may have an isotactec, syndiotactic or atactic structure, and the molecular weight thereof is above about 2,000 g/mole, preferably in the range of from 10,000 to about 1,000,000 g/mole. In particular, preferred embodiments, the molecular weight of the polyolefin segment is in the range from about 10,000 to about 200,000 g/mole. In one aspect of the invention, the functional polymer segment, chemically bonded to the polyolefin segment, is a polymer which is prepared by either free radical polymerization of a free radical polymerizable monomer, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA), styrene or acrylonitrile, or by ring-opening polymerization of a cyclic monomer, such as a lactone, lactam, 2-oxazoline, cyclic ether or mixtures thereof. Non-limitive examples of cyclic monomers which are capable of undergoing ring opening polymerization and which may be used to prepare the functional polymer
segment include, β-propiolactone, β-butyrolactone, δ-valerolactone, glycolide, lactide, ε-caprolactone, α-pyrrolidone, γ-butyrolactam, ε-caprolactam, ethylene oxide, propylene oxide, epichlorohydrin, oxetane, tetrahydrofuran and octamethylcyclotetrasiloxane.

The molecular weight of functional polymer segment is above about 500 g/mole, preferably in the range from about 2,000 to 1,000,000 g/mole, and mostly preferably in the range of from about 10,000 to 200,000 g/mole. The functional polymer segment may comprise from about 1 to about 95 wt. % of the diblock copolymer. However, the functional polymer segment typically comprises form about 5 to about 80 wt. % of the diblock copolymer.

As is well-known, one of the major termination steps in Ziegler-Natta polymerization of α-olefins is β-proton elimination, especially at elevated temperature. This reaction creates a double bond at the end of each polyolefin chain. This phenomena is quite general in all commercial polyolefins, including polyethylene, isotactic polypropylene, poly(1-butene), poly(1-octene) and their copolymers. It also occurs in the cationic polymerization of isobutylene. It is this termination step which results in the formation of the chain-end unsaturated polyolefin (I), which may include, but which is not limited to, polyethylene, polypropylene, polyisobutylene and poly(ethylene-co-propylene).

The post-treatment of the chain-end unsaturated polyolefin (I) involves hydroboration of the terminally unsaturated group and the interconversion of the resulting borane group to a functional group. Hydroboration reagents which may be used for this reaction contain a boron-hydride species, and include, for
example, diborane, 9-borobicyclo[3,3,1]nonane (9-BBN), dimethyborane, dichlorborane and catecholborane, all of which are reactive to double bonds.

The hydroboration reaction may be performed as described in detail in Chung et al., Macromolecules, **27**, 7533-7537, (1994), the disclosure of which is incorporated herein by reference in its entirety. In one aspect of the invention, the hydroboration is performed by adding a hydroboration reagent to unsaturated polyolefin and heating the resulting mixture to dissolve the polyolefin and to effect the hydroboration reaction. The heating is performed at about 65°C for about 3 hours, followed by cooling to precipitate the borated polymer from solution. In one preferred aspect, 9-BBN or dimethylborane, is used as the hydroboration reagent.

In one embodiment, the borane-terminated polyolefin (II) which is formed during the hydroboration reaction is subjected to oxidation by reaction with oxygen in the presence of a free radical polymerizable monomer, such as methyl methacrylate (MMA), ethyl methacrylate (EMA), vinyl acrylate (VA), butyl acrylate (BA) and styrene. The reaction scheme is illustrated below:
The reaction usually takes place by slowly adding oxygen to a polymer solution containing polylefin, monomer and solvent at ambient temperature. Usually, oxygen insertion takes place at the B-C bond connecting the polymer chain and the borane group to produce peroxyborane (C-O-O-B). The peroxyborane behaves very differently form regular benzoyl peroxides and consequently decomposes by itself even at ambient temperature. The decomposition reaction follows the homolytic cleavage of peroxide to generate an alkoxy radical (C-O•) and a borinate radical (B-O•) which is relatively stable due to the back-donating of electron density to the empty p-orbital of boron. The alkoxy radical, produced by the homolytic cleavage of peroxyborane, is very reactive and can then be used for the initiation of radical polymerization. However, the borinate radical may form a weak and reversible bond with the growing chain end during the polymerization reaction. Upon the dissociation of an electron pair in the resting state, the growing
chain end can then react with monomers to extend the polymer chain. The radical polymerization can be terminated by precipitating the polymer mixture in methanol (MeOH). The product, isolated by filtration and washed with MeOH, is subjected to the fractionalization. The resulting polymer is illustrated as product V in the above equation.

The borane-terminated polyolefin (II) also can be interconverted to a series of intermediate telechelic polyolefins (III), which contain a polar functional group, such as -OH, -NH₂, -CHO or -I. The interconversion may be accomplished, for example, by following the procedures described in H. C. Brown, Organic Synthesis via Boranes; Wiley-Interscience: New York (1975). More specifically, the boron terminal group may be oxidized using NaOH/H₂O₂ reagents at about 40°C for about 3 hours to convert the borane group to a hydroxy group. The polar functional group in the intermediate polyolefin (III) is then used as the active site for the ring-opening polymerization of a cyclic functional monomer, such as a lactone, lactam, cyclic ether or 2-oxazoline. The ring opening polymerization may be conducted by contacting the telechelic intermediate polyolefin (III) with the cyclic monomer neat, or in solution or slurry in an appropriate organic medium, such as toluene. The ring opening polymerization may be conducted at a temperature from about 0 to about 100°C, and for a period of from about 30 minutes to about 12 hours. Preferably the ring opening polymerization is conducted at or about room temperature for a period of from about 1 to about 6 hours, e.g., 3 hours. The ring-opening polymerized polymer is chemically bonded to the chain end of the polyolefin. One example of a diblock copolymer formed
in accordance with the present invention is polypropylene-f-polycaprolactone, the preparation of which is illustrated schematically below:

\[ \text{PP} \xrightarrow{\text{BuLi}} \text{PP-CH-O-AlEt}_2 \xrightarrow{\epsilon-CL} \text{PP-CH-O-C-PCL} \]

In the above reaction scheme, PP represents a polypropylene segment and PCL represents a polycaprolactone segment. The two segments are chemically linked through an ester functional linkage. The hydroxy group in the intermediate functionalized polypropylene is converted to an Al alkoxide group which is then used to initiate the ring opening polymerization of \( \epsilon \)-caprolactone. Preferably, the conversion of the hydroxy group to the Al alkoxide group would be accomplished by means of a metallation or graft-from reactions using suspension conditions with PP fine particles slightly swollen in a solvent, such as toluene. Amorphous regions should be completely soluble in the toluene, but crystalline domains would be unaffected. Being a chain end in the PP helix, the hydroxy functional group would preferentially be in the amorphous domain and hopefully would be more accessible to reaction.
The polyolefin diblock copolymers of the present invention are useful in their own right, ranging from elastomeric to thermoplastic polymer compositions, and are particularly useful as interface modifiers for improving adhesion of polyolefins to substrates and as compatibilizers in polyolefin blends and composites. Accordingly, one aspect of the invention comprises a method of compatibilizing a mixture containing (a) a polyolefin, prepared by transition metal coordination polymerization of an α-olefin, such as ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, styrene and their mixtures, and (b) a functional polymer, such as an acrylic polymer, methacrylic polymer, polyvinyl acetate, polyvinyl chloride, polyacrylonitrile, polyester, polyamide, polyimide, polyether, polycarbonate, polyurethane or cellulose, which is incompatible with polyolefins, which method comprises adding to the mixture a compatibilizing amount, typically from about 0.5 to about 10 % by weight, based on the weight of the compatibilized mixture, of a diblock copolymer as described above.

In polyolefin composites with fillers or fibers, such as carbon black, carbon fibers or glass fibers, the diblock copolymers of the present invention provide good adhesion between the polyolefin matrix and the fillers or fibers. More specifically, the polar groups in functional polymer segment of the diblock copolymer located at the interface between the polyolefin matrix and the fillers or fibers offer strong interaction to filler or fiber surface whereas the polyolefin segment of the diblock copolymer interacts or co-crystallizes with the polyolefin matrix. The same phenomenon is also observed when polyolefins are coated on an otherwise incompatible substrate. Accordingly, the invention also provides a method for
producing polyolefin/substrate laminate products, such as polypropylene/aluminum and polypropylene/glass, wherein the present polyolefin diblock copolymers are applied at the interface to provide adhesion between a polyolefin film or coating and a substrate.

The following examples are illustrative of the principles and practice of this invention, and are not intended to be limitative thereof.

**Example 1**

**Synthesis of Chain-end Unsaturated PP**

To a Parr 450 ml stainless autoclave equipped with a mechanical stirrer, 100 ml of toluene and 0.5 g (2.5 mmol in Al) methylaluminoxane (MAO) (30 wt.% in toluene) were placed in an argon-filled dry-box. The sealed reactor was then moved out from the dry box and purged with propylene gas. After the temperature reached 80°C, a catalyst solution of 2.09 mg (5 μmol) of ethylene bis(indeny)lizirconium dichloride (Et(Ind)₂ZrCl₂) in 2 ml of toluene was added under propylene pressure to initiate the polymerization. Additional propylene was fed continuously into the reactor to maintain a constant pressure of 10 psi during the whole course of the polymerization. After 140 min, the reaction was terminated by addition of 100 ml of dilute HCl solution in MeOH. The resulting polymer was isolated by filtration and was washed completely with MeOH and dried under vacuum at 50°C for 8 hrs. About 38.0 g of somewhat sticky PP polymer (Mp = 61.7°C; Mw = 5,700 g/mole, Mw/Mn = 1.68; mm = 55.8%) was obtained. The chain end unsaturation was observed by IR, ¹H NMR and ¹³C NMR.
Example 2

Synthesis of Chain-end Unsaturated PP

The procedure described in Example 1 was carried out for the polymerization of propylene, except that the polymerization temperature was 50°C (instead of 80°C) and that the polymerization was terminated by the addition of 100 ml of dilute HCl solution in MeOH after 60 min. (instead of 140 min.). After washing and drying, about 31.4 g of PP fine powder (Mp = 121.1°C; Mw = 12,700 g/mole; Mw/Mn = 1.73; mm = 87.8%) was obtained. The chain end unsaturation was observed by IR, ¹H NMR and ¹³C NMR.

Example 3

Synthesis of Chain-end Unsaturated PP

The procedure described in Example 1 was carried out for the polymerization of propylene, except that the polymerization temperature was 30°C (instead of 80°C) and that the polymerization terminated by the addition of 100 ml of dilute HCl solution in MeOH after 60 min. (instead of 140 min.). After washing and drying, about 33.7 g of PP fine powder (Mp = 138.7°C; Mw = 25,400 g/mole; Mw/Mn = 1.70; mm = 92.8%) was obtained. The chain end unsaturation was observed by IR, ¹H NMR and ¹³C NMR.

Example 4

Synthesis of Chain-end Unsaturated PP

To a Parr 450 ml stainless autoclave equipped with a mechanical stirrer, 100
ml of toluene and 1.5 g (7.5 mmol in Al) methylaluminoxane (MAO) (30 wt.% in toluene) were placed in an argon- filled dry-box. The sealed reactor was then moved out from the dry box and purged with propylene gas. At room temperature, a catalyst solution of 2.09 mg (5 μmol) of Et(Ind)_2ZrCl_2 in 2 ml of toluene was added under propylene pressure to initiate the polymerization. Additional propylene was fed continuously into the reactor to maintain a constant pressure of 29 psi during the whole course of the polymerization. After 60 min, the reaction was terminated by addition of 100 ml of dilute HCl solution in MeOH. The resulting polymer was isolated by filtration and was washed completely with MeOH and dried under vacuum at 50°C for 8 hrs. About 47.5 g of PP polymer was obtained. Due to the high molecular weight polymer, no chain-end unsaturation was detected by IR, ^1^H NMR.

Example 5

Synthesis of Chain-end Unsaturated PP

About 90 ml of toluene was charged into a Parr 450 ml stainless autoclave equipped with a mechanical stirrer. The sealed reactor was then purged with propylene gas and then heated up to 85°C before adding a pre-mixed catalyst solution containing 0.5 g (2.5 mmol) of (TiCl_3, AA) and 1.84 g (15 mmol) of diethyl aluminum chloride (AlEt_2Cl) in 20 ml of toluene. A constant propylene pressure of 6 psi was continuously fed into the reactor during the polymerization. After 30 min, the reaction was terminated by addition of 100 ml of dilute HCl
solution in MeOH and the resulting polymer was isolated by filtration. The polymer was washed completely with MeOH and dried under vacuum at 50°C for 8 hrs. About 9.59 g of PP polymer was obtained. Due to high molecular weight polymer, no chain-end unsaturation was detected by IR, 1H NMR.

Example 6

Synthesis of Chain-end Unsaturated PE

To a parr 450 ml stainless autoclave equipped with a mechanical stirrer, 100 ml of toluene and 0.315 g (1.57mmol in Al) methylaluminoxane (MAO) (30 wt.% in toluene) were placed in an argon-filled dry-box. The sealed reactor was then moved out from the dry box and purged with ethylene gas. After the temperature reached 80°C, a catalyst solution of 2.09 mg (5μmol) of Et(Ind)₂ZrCl₂ in 2 ml of toluene was added under ethylene pressure to initiate the polymerization. Additional ethylene was continuously fed into the reactor to maintain a constant pressure of 10 psi during the whole course of the polymerization. After 60min, the reaction was terminated by addition of 100 ml of dilute HCl solution in MeOH. The resulting polymer was isolated by filtration and was washed completely with MeOH and dried under vacuum at 50°C for 8 hrs. 5.93g PE polymer (Mp =131.7°C; Mw = 66,300 g/mole; Mw/Mn = 2.54) was obtained.

Example 7

Synthesis of Chain-end Unsaturated PE

To a parr 450 ml stainless autoclave equipped with a mechanical stirrer, 100
ml of toluene and 1.5 g (7.5 mmol in Al) methylaluminoxane (MAO) (30 wt.% in toluene) were placed in an argon-filled dry-box. The sealed reactor was then moved out from the dry box and purged with ethylene gas. After the temperature reached 30°C, a catalyst solution of 2.09 mg (5 μmol) of Et(Ind)₂ZrCl₂ in 2 ml of toluene was added under ethylene pressure to initiate the polymerization. Additional ethylene was fed continuously into the reactor to maintain a constant pressure of 45 psi during the whole course of the polymerization. After 60 min, the reaction was terminated by addition of 100 ml of dilute HCl solution in MeOH, The resulting polymer was isolated by filtration and was washed completely with MeOH and dried under vacuum at 50°C for 8 hrs. 3.22 g PE polymer (Mp 138°C) was obtained.

**Example 8**

**Hydroboration Reaction of Chain-end Unsaturated PP**

To a 250 ml glass flask equipped with a magnetic stirr bar, 4.0 g chain-end unsaturated PP (obtained from Example 2) was placed in a suspension of 100 ml dry, O₂-free tetrahydrofuran (THF) in an argon-filled dry box, the polymer was hydroborated by the addition of 5.0 ml of 0.5 M lithium dimethylborohydride solution in hexane and 0.33 ml of trimethylchlorosilane. The polymer slurry was stirred overnight in dry box at room temperature, and was then filtered, washed with dry, O₂-free IPA and dried in a vacuum. The resulting polymer product was chain-end borane containing polypropylene.
Example 9

Oxidation Reaction of Borane Terminated PP

About 2.0 g of borane terminated PP (obtained by Example 8) was placed in a suspension of 50 ml dry, \( \text{O}_2 \)-free THF in a dry box. The sealed reactor was moved out of the dry box and purged with nitrogen gas. To the polymer slurry, a solution containing 0.4 g of NaOH in 2 ml \( \text{H}_2\text{O} \) and 0.5 ml MeOH purged by \( \text{N}_2 \) was added at room temperature, followed by the dropwise addition of 1.6 ml of 30\% oxygen-free \( \text{H}_2\text{O}_2 \) was added dropwise at 0°C. The oxidation was performed at 40°C for 6 hrs. before being terminated by pouring the reaction mass into 100 ml of MeOH. The resulting polymer solid was filtered, and was then refluxed in 100 ml of MeOH for 2 hrs before distilling off 10 ml of MeOH. The resulting hydroxylated PP was then recovered by filtration and was dried in vacuum oven at 50°C for 8 hrs. Chain-end OH groups in the PP were observed by IR, \(^1\text{H}\) NMR.

Example 10

Amination Reaction of Borane Terminated PP

About 2.0 g of borane group terminated PP (obtained by Example 8) was placed in a suspension of 50 ml dry, \( \text{O}_2 \)-free THF in a dry box. The sealed reactor was moved out of the dry box and purged with nitrogen gas. Hydroxylamide sulfonic acid (0.5 g) was added to the polymer slurry at room temperature under \( \text{N}_2 \) purge. The amination reaction was carried out at 50°C for 8 hrs and was then terminated by adding 20 ml of \( \text{H}_2\text{O} \). After filtration and several washings with acetone, the polymer powder was dried in vacuum oven at 50°C for 8 hrs. Chain-
end NH₂ groups in PP polymer were observed by IR, ¹H NMR.

Example 11

Synthesis of PP-b-PMMA Diblock Copolymer

Borane-terminated polypropylene (13.3 g, obtained by Example 8) was placed in a suspension of 80 g dry uninhibited MMA with 80 ml THF in a sealed, opaque flask. The reaction was initiated by injecting 10.8 ml dry O₂ over a period of 5 hours. After stirring the mixture at ambient temperature for 16 hours, the reaction was terminated by addition of 100 ml methanol. The precipitated polymer was filtered and then fractionated by acetone and hapten extractions in Soxhlet apparatus under N₂ for 24 hours, respectively. The soluble fractions were isolated by vacuum-removal of solvent. The insoluble polymer was PP-b-PMMA, which was completely soluble in xylene at elevated temperatures. The polymer structures and compositions were confirmed by IR, ¹H NMR, GPC and DSC studies. Several similar runs were performed using a similar reaction procedure. The experimental results are summarized in the following table. The overall yield of diblock copolymer was between about 60 and 80%. The yield of PP homopolymer was between about 20 and 40%.
A Summary of PP-b-PMMA Copolymers

<table>
<thead>
<tr>
<th>Reaction Conditions</th>
<th>Fractionalization Product</th>
<th>Mole% MMA in Copolymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP* (g)</td>
<td>MMA (g)</td>
<td>Solvent (ml)</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>THF / 5</td>
</tr>
<tr>
<td>0.5</td>
<td>5</td>
<td>benzene / 5</td>
</tr>
<tr>
<td>13.3</td>
<td>80</td>
<td>THF / 80</td>
</tr>
</tbody>
</table>

* P sample with Mn = 13,000 and Mw/Mn = 1.48

** This fraction is insoluble in acetone and heptane at room temperature, but is soluble in xylene at elevated temperatures

Example 12

Synthesis of Poly(propylene-b-t-butyl methacrylate)

In an argon filled dry-box, 0.6 g of borane-terminated polypropylene from Example 8 was placed in a suspension with 5 g of t-butyl methacrylate (dried over CaH₂ and vacuum distilled) in a septa equipped flask. After stirring for 1/2 hour in the dry-box, the flask was taken out of the box and stirred at room temperature. Air was very slowly diffused into the flask. Within 8 hours, the suspension viscosity had increased noticeably. By 24 hours, the reaction was stopped and the suspension had become a translucent solid. The solid was broken up and stirred in MeOH for 1 hour and then filtered. The polymer was extracted with acetone in a Soxhlet extractor for 18 hours. The acetone soluble fraction yielded 0.199 g. The
acetone insoluble fraction yielded 1.12 g of white solid after drying under vacuum. 

$^1$H NMR in $d_{10}$-xylene of the acetone insoluble fraction indicated by integration that the material was 45 mole % t-butyl methacrylate in polypropylene.

**Example 13**

**Synthesis of Poly(propylene-b-vinyl acetate)**

In an argon filled dry-box, 1 g of borane-terminated polypropylene from Example 8 was placed in a suspension with 10 g of vinyl acetate (dried over CaH$_2$ and vacuum distilled) in a septa equipped flask. After stirring for 1/2 hour in the dry-box, the flask was taken out of the dry-box and stirred at room temperature. Immediately, 1 ml of dry oxygen was injected slowly into the flask with a gas tight syringe. The solution was stirred at room temperature for 16 hours before terminating the reaction with the addition of 10 ml methanol. The precipitated polymer solid was filtered, and was then extracted with acetone in a Soxhlet extractor for 18 hours. The acetone soluble fraction yielded 1.18 g of white solid after drying under vacuum. 

$^1$H NMR in $d_{10}$-xylene of the acetone insoluble fraction indicated by integration that the material was 18 mole % vinyl acetate in polypropylene.

**Example 14**

**Synthesis of PP-b-PCL Diblock Copolymer**

The hydroxy-terminated PP (0.7 g), obtained from Example 9, was dispersed in a dry, degassed toluene solution in a dry box. The hydroxy-terminated
PP was then metallated with excess n-butyllithium to form the lithium alkoxide. The polymer was stirred for 12 hours before it was isolated by filtration and repeatedly washed and filtered in toluene. The powdery solid was then placed in toluene as a slurry solution and reacted with a 3 molar equivalents of diethylaluminum chloride for 12 hours to form PP-aluminum alkoxide (PP-OAlEt₂). Again, the polymer was isolated by repeated filtration and washing in toluene, followed by filtration and washing in hexane.

The cyclic ester caprolactone (Aldrich Chemical) was purified by drying over calcium hydride and distilling under reduced pressure. In the dry box, 5 g of the purified caprolactone was added to a slurry of 0.7 g of PP-OAlEt₂ in 20 ml of toluene. The reaction mixture was stirred at room temperature for 3 hours before terminating the reaction by adding 10 ml MeOH. The polymer mixture was isolated by precipitation into acidified MeOH. The polymer was extracted with hot acetone in a Soxhlet apparatus under N₂ for 48 hours to remove any caprolactone homopolymer, which is soluble in acetone. After isolation of both fractions, 0.13 g of acetone soluble polylactone homopolymer and 1.02 g acetone insoluble PP-b-PCL diblock copolymer (Mw = 19,700 g/mole; Mw/Mn = 1.74) were obtained. The polymer structures were confirmed by IR, ¹H NMR.

Example 15

Synthesis of PP-b-PCL Diblock Copolymer

A reaction procedure similar to that of Example 14 was used for the synthesis of PP-b-PCL, except that the hydroxy-terminated PP that was used as the
starting material was prepared from a higher molecular weight chain end unsaturated PP (obtained from Example 3, rather than from Example 2) than was used in Example 14. For this example, 10 g of hydroxy-terminated PP, derived from chain-end unsaturated PP having a Mw of 25,400 g/mole, was hydroborated with 9-BBN generally as described in Example 8. The chain end hydroxy polymer was metallated with a 3 molar equivalent of diethylaluminum chloride for 12 hours to form the PP-aluminum alkoxide. The polymer was isolated by repeated filtration and washing in toluene, followed filtration and washing in hexane. The aluminum alkoxide functionalized polymer was then placed in a slurry of 80 g of caprolactone and 80 ml of toluene. The reaction was stirred at room temperature for 18 hours, at which time the reaction was terminated by the addition of MeOH. The polymer was isolated by precipitation into 800 ml of MeOH. The polymer was extracted with hot acetone in a Soxhlet apparatus under N₂ for 48 hours to remove any caprolactone homopolymer. After the isolation and drying, 1.27 g of acetone soluble lactone homopolymer and 16.98 g acetone insoluble polymer (Mw = 31,400 g/mole; Mw/Mn = 1.69) were obtained.

Example 16

Synthesis of PE-b-PCL Diblock Copolymer

Chain end unsaturated PE prepared by Et(Ind)₂ZrCl₂/MAO catalyst system in Example 6 was subjected to hydroboration and oxidation reactions to form powdered hydroxy group terminated PE. About 1 g of the hydroxylated PE powder was suspended in a dry, degassed toluene solution in a dry box and then metallated with excess n-
butyllithium to form the PE-lithium alkoxide. The polymer was stirred for 12 hours before it was isolated by filtration and repeatedly washed and filtered in toluene followed by the same procedure in hexane. The resulting powdery solid was placed in a slurry of fresh toluene and reacted with a 3 molar equivalents of diethylaluminum chloride for 12 hours to form PE-aluminum alkoxide (PE-OAlEt$_2$). The resulting PE-OAlEt$_2$ was isolated by repeated filtration and washing in toluene, followed by filtration and washing in hexane. In the dry box, 15 g of caprolactone was added to a slurry of 1 g of PE-OAlEt$_2$ in 15 ml of toluene. The reaction was stirred at room temperature for 18 hours, at which time the reaction was terminated by the addition of MeOH. The resulting diblock PE-b-PCI copolymer was isolated by precipitating into MeOH. The polymer was extracted with hot acetone in a Soxhlet apparatus under N$_2$ for 48 hours to remove any caprolactone homopolymer.

While the invention has been described with reference to specific embodiments thereof, it will be appreciated that numerous variations, modifications, and embodiments are possible, and accordingly, all such variations, modifications, and embodiments are to be regarded as being within the spirit and scope of the invention.
What is claimed is:

1. A polyolefin diblock copolymer having the formula:

   \[(\text{polyolefin segment})-f-(\text{functional polymer segment})\]

   wherein \(f\) is a chemical linkage selected from the group consisting of ether, ester and amide group linkages;

   said polyolefin segment having been prepared by transition metal coordination polymerization of at least one \(C_2-C_{12}\) \(\alpha\)-olefin, and having a molecular weight of from about 10,000 to about 1,000,000 g/mole; and

   said functional polymer segment having been prepared by free radical polymerization of a free radical polymerizable monomer or by ring-opening polymerization of at least one cyclic monomer, and having a molecular weight of from about 2,000 to about 1,000,000 g/mole.

2. The polyolefin diblock copolymer of Claim 1, wherein said at least one \(C_2-C_{12}\) \(\alpha\)-olefin is selected from the group consisting of ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, styrene and mixtures thereof.

3. The polyolefin diblock copolymer of Claim 1, wherein said polyolefin segment has an isotactic, syndiotactic or atactic structure.
4. The polyolefin diblock copolymer of Claim 1, wherein said functional polymer segment comprises from about 5 to about 80 wt. % of said diblock copolymer.

5. The polyolefin diblock copolymer of Claim 1, wherein said functional polymer segment has been prepared by free radical polymerization of a free radical polymerizable monomer.

6. The polyolefin diblock copolymer of Claim 5, wherein said polymerizable monomer is selected from the group consisting of methyl methacrylate, ethyl methacrylate, butyl acrylate, vinyl acrylate, styrene and mixtures thereof.

7. The polyolefin diblock copolymer of Claim 1, wherein said functional polymer segment has been prepared by ring opening polymerization of at least one cyclic monomer.

8. The polyolefin diblock copolymer of Claim 7, wherein said at least one cyclic monomer is selected from the group consisting of lactones, lactams, 2-oxazolines, cyclic ethers and mixtures thereof.

9. A process for the preparation of polyolefin diblock copolymers having the general formula:
(polyolefin segment)-f-(functional polymer segment),

wherein f represents a chemical linkage selected from the group consisting of ether, ester and amide group linkages, which comprises:

(a) providing a functionalized polyolefin having the general formula

\[
\begin{align*}
R' \\
\text{polyolefin-CH-F}
\end{align*}
\]

wherein R' is H, C_1-C_{20} alkyl, phenyl or alkyl-substituted phenyl and F is a polar functional group; and

(b) contacting a cyclic monomer capable of undergoing ring opening polymerization with said functionalized polyolefin under ring opening polymerization reaction conditions, whereby said cyclic monomer undergoes ring opening polymerization using said polar functional group in said functionalized polyolefin as a polymerization initiating active site.

10. The process of Claim 9 wherein said functionalized polyolefin is prepared by:

(i) forming a chain-end unsaturated polyolefin homopolymer or copolymer by transition metal coordination polymerization of at least one olefin C_2-C_{12} \( \alpha \)-olefin;

(ii) hydroboring said chain-end unsaturated polyolefin with a boron hydride species hydroboration reagent reactive to the double bond in said chain-end unsaturated polyolefin to provide a polyolefin having a terminal borane group; and
(iii) converting said borane group to a functional group selected from the

group consisting of -OH, -NH₂, -CHO and halide.

11. The process of Claim 10, wherein said at least one α-olefin is selected from

the group consisting of ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-

octene, styrene and mixtures thereof, and wherein said hydroboration reagent is

selected from the group consisting of diborane, 9-borobicyclo[3,3,1]nonane,

dimethylborane, dichloroborane, catecholborane and mixtures thereof.

12. The process of Claim 9, wherein said cyclic monomer capable of undergoing

ring opening polymerization is selected from the group consisting of lactones,
lactams, 2-oxazolines, cyclic ethers and mixtures thereof.

13. The process of Claim 12, wherein said ring opening polymerization is

conducted at room temperature.

14. The process of Claim 12, wherein said ring opening polymerization is

conducted neat or in solution or in slurry.

19. The process of Claim 9, wherein said functionalized polyolefin is prepared

by:

(i) forming a chain-end unsaturated polyolefin homopolymer or copolymer by

transition metal coordination polymerization of at least one olefin C₂-C₁₂ α-olefin,
(ii) hydroborating said chain-end unsaturated polyolefin with a boron hydride species hydroboration reagent reactive to the double bond in said chain-end unsaturated polyolefin to provide a polyolefin having a terminal borane group;

(iii) converting said borane group to an -OH group; and

(iv) converting the -OH group to a metal alkoxide group.

16. The process of Claim 15, wherein said olefin polymer is polypropylene and said cyclic monomer capable of undergoing ring opening polymerization is ε-caprolactone.

17. A process for the preparation of polyolefin diblock copolymers having the general formula:

\[(\text{polyolefin segment}) - f - (\text{functional polymer segment}),\]

wherein f represents a chemical linkage, which comprises:

(a) providing a polyolefin having a terminal borane group, said polyolefin having the general formula:

\[\text{polyolefin-CH-}R_1 R_2\]

wherein R' is H, C₁-C₂₀ alkyl, phenyl or alkyl-substituted phenyl or alkyl-
substituted phenyl, and \( R_1 \) and \( R_2 \) independently, are \( H \), a halide, a \( C_1-C_5 \) alkoxyde, or a \( C_1-C_{20} \) linear or branched alkyl, cyclic or bicyclic structure;

(b) contacting a monomer capable of undergoing free radical polymerization with said polyolefin having a terminal borane group under free radical polymerization reaction conditions, whereby said monomer undergoes free radical polymerization using said terminal borane group in said polyolefin as the free radical polymerization initiating active site.

18. The process of Claim 17, wherein said polyolefin having a terminal borane group is prepared by:

(i) forming a chain-end unsaturated polyolefin homopolymer or copolymer by transition metal coordination polymerization of at least one olefin \( C_2-C_{12} \) \( \alpha \)-olefin; and

(ii) hydroborating said chain-end unsaturated polyolefin with a boron hydride species hydroboration reagent reactive to the double bond in said chain-end unsaturated polyolefin having a terminal borane group.

19. The process of Claim 18, wherein said at least one \( \alpha \)-olefin is selected from the group consisting of ethylene, 1-propene, 1-butene, 1-pentene, 1-hexene, 1-octene, styrene and mixtures thereof, and wherein said hydroboration reagent is selected from the group consisting of diborane, 9-borobicyclo[3,3,1]nonane, dimethylborane, dichloroborane, catecholborane and mixture thereof.
20. The process of Claim 19, wherein said monomer capable of undergoing free radical polymerization is selected from the group consisting of methyl methacrylate, ethyl methacrylate, vinyl acrylate, butyl acrylate, styrene and mixture thereof.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC(6) : C08F 293/00, 295/00, 297/08
US CL.: 525/268, 279, 288, 296, 310, 316, 317
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED
Minimum documentation searched (classification system followed by classification symbols)
U.S.: 525/268, 279, 288, 296, 310, 316, 317

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

APS
search terms: block copolymers, diene, acrylate, borane, 9-borabicyclo-(3,3,1)-nonane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>X</td>
<td>US 5,401,805 A (CHUNG et al.) 28 March 1995, column 6, lines 41-46.</td>
<td>1-20</td>
</tr>
</tbody>
</table>

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special category of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "B" earlier document published on or after the international filing date
  "L" document which may throw doubt on priority claim(s) or which is cited to establish the publication date of another document or other special reason (as specified)
  "C" document referring to an oral disclosure, use, exhibition or other means
  "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"S" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"V" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

Date of the actual completion of the international search
12 SEPTEMBER 1997

Date of mailing of the international search report
02 DEC 1997

Name and mailing address of the ISA/US
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231
Facsimile No. (703) 305-3230

Authorized officer
IRNA S. ZEMEL
Telephone No. (703) 308-2351

Form PCT/ISA/210 (second sheet)(July 1992)
**INTERNATIONAL SEARCH REPORT**

**Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
   because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:  
   because they relate to part of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:  
   because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☑ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet(1)/July 1992)
BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claim(s) 1-8, drawn to block copolymer.

Group II, claim(s) 9-16, drawn to a process of making a block copolymer.

Group III, claim(s) 17-20, drawn to a method of making a block copolymer.

The inventions listed as Groups I-III do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the block copolymers that contain a polyolefin segment, chemical linkage and a functional polymer segment are known and would have been obvious from teachings of Chung U.S. Patent 5,401,805.