(54) Title: SYNDIOTACTIC POLYPROPYLENE SOLUTIONS AND APPLICATIONS THEREFOR

(57) Abstract

A process for processing solvated syndiotactic polypropylenes having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 in a liquid hydrocarbon at temperatures below 80 degrees C is provided.
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TITLE: SYNDIOTACTIC POLYPROPYLENE SOLUTIONS AND APPLICATIONS THEREFOR

SPECIFICATION

TECHNICAL FIELD

This invention relates to compositions comprising a syndiotactic polypropylene dissolved in a liquid hydrocarbon at a temperature below about 80 degrees C. This invention further relates to the use of such solutions as a stock for the formation of articles.

BACKGROUND OF THE INVENTION

Crystalline polypropylene, whether isotactic or syndiotactic, is not normally soluble in liquid hydrocarbons at ambient temperatures. Hence, any dissolution of polypropylene into a hydrocarbon solvent has been obtained by heating the hydrocarbon solvent to an elevated temperature which is at or above the dissolution temperature of the polypropylene (T_dpp) to dissolve the polypropylene and the solution is maintained at or above this elevated temperature to prevent spontaneous recrystallization of the polypropylene. Portions of the hot solution may then be utilized as stock solution for the formation of fibers of fibrils by continuously feeding the solution to spinerettes or other devices wherein the solution is ejected through an orifice or spinning aperture and by pressure drops or temperature reductions the polypropylene is recrystallized or precipitated from the solution in the form of fibers.
In yet other techniques, a hydrocarbon solution of crystalline polypropylene is obtained by a combination of solvent temperature elevation and continuous solution agitation. In this technique the solvent temperature may be below the dissolution temperature of the polypropylene and the continuous agitation or stirring of the solution prevents the spontaneous recrystallization of the polypropylene which would otherwise occur in the absence of any agitation. Portions of the agitated stock are forced through a spinning aperture and the polypropylene article, such as a fiber, forms upon crystallization of the polypropylene from solution.

Whichever technique is utilized for obtaining the required polypropylene-hydrocarbon solution, it is necessary to heat the hydrocarbon solvent to elevated temperatures in the range of 100-185 degrees C and maintain the stock solution at this elevated temperature while portions of the stock are subjected to a forming process. This necessity increases both the cost and hazards of a process for forming fibers from crystalline polypropylene. Cost is increased, both capital and operational, because of the need for heat exchange equipment to supply the heat required for formation and maintenance of the polypropylene in solution. Hazards are increased because hydrocarbon solvents are volatile and their vapor pressure is greatly increased by elevated temperature. Further, even after the polypropylene has formed an article, such as a fiber, the portion of solvent from which it is formed is generally still at a temperature where process means for safe containment and recapture of the solvent for reuse in the process must be provided.

The above-mentioned difficulties in processing crystalline polypropylene could substantially be
reduced or eliminated if a polypropylene-hydrocarbon solution could be devised in which the polypropylene does not spontaneously recrystallize at a temperature at or well below the process in use. Such lower temperature crystalline polypropylene-hydrocarbon solutions could be utilized to produce articles, such as spinning stock to produce polypropylene fibers by wet or dry spinning techniques.

SUMMARY OF THE INVENTION

It has been discovered that crystalline polypropylene having certain characteristics is capable of existing in solution in a liquid hydrocarbon solvent at temperatures below the dissolution temperature of typical commercial isotactic polypropylenes. The polypropylene solution can be used at or near ambient or room temperatures. Such room temperature hydrocarbon polypropylene solutions are prepared by dissolving in a liquid hydrocarbon solvent a crystalline polypropylene having a ratio of racemic mole fraction to meso mole fraction of 18:1 or less. Upon adding such a polypropylene to a hydrocarbon solvent in an amount to provide a desired weight percent solution, the solvent may be heated to an elevated temperature to hasten dissolution of the polypropylene and thereafter the solution cooled to a temperature below the dissolution point for isotactic polypropylene, preferably below about 80 degrees C.

The hydrocarbon solutions of such syndiotactic polypropylene may be used to prepare polypropylene coatings or fibers by a solvent spinning process. Since the solution of polypropylene is at or about ambient temperatures, the economics and safety of the process are improved.
For convenience sake, the solutions of syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of 18:1 or less dissolved in a hydrocarbon at a temperature less than the usual dissolution temperature for commercial polypropylene, preferably about 80 degrees C or less, more preferably at about 70 degrees C or less, more preferably about 30 degrees C or less, even more preferably at room or ambient temperature, will be referred to as "lower temperature sPP solutions."

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Polypropylenes suitable for use in preparing lower temperature sPP solutions include those having a ratio of racemic mole fraction to meso mole fraction of 18:1 or less. In a preferred embodiment the syndiotactic polypropylene has an Mw of about 500,000 or more.

Such syndiotactic polypropylenes may be prepared by polymerizing propylene with a catalyst system comprising a stereorigid metalloocene and an activator compound wherein (a) the stereorigid metalloocene comprises a Group TVB metal compound having two cyclopentadienyl ligands (Cp and Cp*) which are stearically different from each other and each cyclopentadienyl ligand is structurally bridged to each other by a bridging group which imparts stereorigidity to the cyclopentadienyl ligands, the ligands satisfying the other valence requirements of the transition metal of the metalloocene compound being hydrocarbyl or halogen radicals, and (b) the activator compound is an alumoxane or an ionic compound of the formula [L'H]+[BAR_1AR_2X_3X_4]^− wherein

L' is a neutral Lewis base;
H is a hydrogen atom;
[L'-H]^+ is a Bronsted acid;
B is boron in a valence state of 3; 
$\text{Ar}_1$ and $\text{Ar}_2$ are the same or different 
aromatic or substituted-aromatic hydrocarbon radicals 
containing from about 6 to about 20 carbon atoms; and 

$X_3$ and $X_4$ are radicals selected, 

independently, from the group consisting of 
hydride radicals, halide radicals, with the proviso that $X_3$ and 
$X_4$ will not be halide at the same time, hydrocarbyl radicals 
containing from 1 to about 20 carbon atoms, 

substituted-hydrocarbyl radicals, wherein one or more 
of the hydrogen atoms is replaced by a halogen atom, 

containing from 1 to about 20 carbon atoms, 
hydrocarbyl-substituted metal (organometalloid) radicals wherein each hydrocarbyl substitution contains 

from 1 to about 20 carbon atoms and said metal is 

selected from Group IV-A of the Periodic Table of the 
elements and the like.

With respect to the stereorigid metalloocene 

compound, at least one of the cyclopentadienyl ligands 

thereof is a substituted cyclopentadienyl group wherein 
1 to 4 of the ring positions is substituted by a 

hydrocarbyl mono or di radical having 1-20 carbon atoms 

and such hydrocarbyl radical may form a fused ring 

system. A pattern of ring substitution is chosen to 

provide that the two cyclopentadienyl ligands have 

substantially different stearic bulk one from another. 

In order for the catalyst system to produce 
syndiotactic polypropylene the cyclopentadienyl ligands 

must be stearically different. Thus, by "stearic 
difference" of "stearically different" as used herein, 
it is intended to imply a difference between the 

stearic characteristics of the $\text{Cp}$ and $\text{Cp}^*$ rings that 
renders each to be symmetrical with respect to the A' 
briding group but different with respect to each other 

that controls the approach of each successive monomer 

unit that is added to the polymer chain. The stearic
difference between the Cp and Cp* rings acts to block the approaching monomer from a random approach such that the monomer is added to the polymer chain in the syndiotactic configuration.

Suitable metallocenes include isopropyl (cyclopentadienyl) (fluorenyl) hafnium dichloride and diphenyl methylene (cyclopentadienyl) (fluorenyl) zirconium dichloride.

Catalyst systems capable of producing high molecular weight syndiotactic polypropylenes which have been found to be and remain soluble in normally liquid hydrocarbons at ambient temperature, i.e. 10 - 35 degrees C, are described in commonly owned copending U.S. Application Serial No. 07/582,702 and in U.S. Patent No. 4,892,851.

Preferred syndiotactic polypropylenes exhibiting the hydrocarbon solubility property herein discovered possess a weight average molecular weight of at least 500,000, and preferably at least 700,000, even more preferably 1,000,000 or more. Accordingly, the conditions of time, temperature, pressure and choice of catalyst system for polymerization are chosen to yield production of such high molecular weight syndiotactic polypropylene. The selection of suitable polymerization condition is well within the skill that is ordinary in the polypropylene polymerization art.

Catalyst systems comprised of isopropyl (cyclopentadienyl) (fluorenyl) hafnium dichloride and an alumoxane and of diphenyl methylene (cyclopentadienyl) (fluorenyl) zirconium dichloride and an alumoxane are preferred for the production of the requisite syndiotactic polypropylene. The polymerization may be accomplished by adding such
catalyst system to liquifed propylene -- the propylene being under sufficient pressure to maintain it at a liquifed state at the temperature chosen for reaction, the reaction temperature typically being in a range of 10 to 70 degrees C, preferably 40 to 60 degrees C.

Hydrocarbon solution of syndiotactic polypropylene having the requisite physical/chemical properties as herein described can be prepared to higher polymer concentrations if desired. Preferably the concentration of dissolved polymer should be kept below that concentration at which the viscosity of the ambient temperature solution would pose difficulties in a solvent spinning process.

Although the invention has been illustrated with decalin as the hydrocarbon solvent, any aliphatic or aromatic hydrocarbon which is liquid at the desired use temperature below 80 degrees C or so may be used. Such hydrocarbons can be linear, branched and/or cyclic hydrocarbons or mixtures thereof, such as nonane, decane, undecane, dodecane, tetrahydronaphthalene or aromatics such as xylene. a class of preferred solvents are those having a melting point below about 20 degrees C.

For solvent spinning purposes the hydrocarbon selected should have a relative high vapor pressure to permit its easy removal and recovery from the polypropylene fiber after fiber formation such as by passing hot air over the formed fiber or by subjecting the fiber to a reduced pressure to vaporize and recover the solvent form the fiber in a dry spinning technique.

For use in a wet spinning technique, one where after fiber formation the fiber is contacted with a non-solvent for the polypropylene in which the hydrocarbon solvent is itself miscible, the hydrocarbon
chosen as the solvent should have a boiling point sufficiently different from the non-solvent to permit their ready separation by distillation techniques.

The lower temperature sPP solutions can be used in a variety of situations. For example, the sPP could be dissolved is a liquid hydrocarbon, such as wax or oil, as a viscosity modifier, drag reducer, a modifier for fuels and the like. These lower temperature sPP solutions could also be used in coating or laminating applications where a coating or layer of syndiotactic polypropylene on a substrate is desired. Likewise these could also be functionalized in low temperature solutions to give new and desirable polymers. For example maleic anhydride (MA) typically moves from the solid to the gas phase without becoming a liquid (sublines) when heated. Thus, it is difficult to graft MA onto polypropylene that must be heated. The instant lower temperature sPP solutions could be utilized to provide a process for producing sPP-g-MA at lower temperatures.

The lower temperature sPP solutions are preferably utilized at temperatures below the typical dissolution temperature of commercial polypropylene, preferably below about 100 degrees C, more preferably about 70 degrees C or below, even more preferably 30 degrees C or below. Particularly Preferred embodiments include utilizing the lower temperature sPP solutions at temperature of 25 degrees C and below or zero degrees C and below.

The sPP can be dissolved in any liquid hydrocarbon. Preferred examples include oil, wax, diesel fuel, hexane, decalin, xylene, decane, gasoline, jet fuels, lubricating oils and the like. Solvents such as decalin, xylene, decene, hexene, and other
aliphatics having 5 to 20 carbon atoms are Preferred for some embodiments including solution spinning, film blowing, laminating, coating, or other forming applications where force or energy is applied to a solution to form an article. Hydrocarbons such as oil, gasoline, wax, diesel fuel and the like are Preferred when the SPP is a modifier or the like.

The syndiotactic polypropylene is preferably present in the liquid hydrocarbon at least about 0.0001 weight percent, more preferably at least about 0.5 weight percent, even more preferably at least about 5 weight percent, more preferably at least about 20 weight percent. For solution spinning processes and forming articles higher weight percents such as at least 5 wt%, at least 20 wt.% even at least 30 wt. % may be preferred, while lower weight percents such as 0.001 wt % or 0.5 wt% may be preferred for modifier type applications. Likewise, the syndiotactic polypropylenes are preferably at least about 80 percent soluble, preferably at least 90 % soluble, even more preferably 98 to 100 percent soluble in the liquid hydrocarbon. Solubility is, of course, dependent on the particular hydrocarbon and the solution temperature. Routine tests can be used to determine what the solution conditions and temperatures should be for a particular desired composition.

The syndiotactic polypropylene preferably has a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1, preferably about 12:1 to about 1:1; more preferably between about 12:1 to about 10:1. The melting point of the syndiotactic polypropylene is about 120 degrees C or less, preferably 111 degrees C or less.

EXAMPLES
Syndiotactic polypropylene was prepared from three catalyst systems:

(1) isopropyl(cyclopentadienyl)(flourenyl)HfCl₂ and methylalumoxane;

(2) Diphenylmethylenecyclopentadienyl)(flourenyl)ZrCl₂ and methyl alumoxane; and

(3) Ethyl(indenyl)(cyclopentadienyl) ZrCl₂ and methyl alumoxane

The polymerizations were conducted in bulk in liquified propylene at 60 degrees C for 1 hour, except for the zirconocenes which were conducted at 40 degrees C for one-half hour. The Al:transition metal ratio of each catalyst system was about 270:1 for the hafnocene and 240:1 for the zirconocenes.

Polymer I was produced with the hafnocene (10 mg metalloocene and 3 ml 10 wt% MAO). Polymer II was produced with the zirconocene (4 mg metalloocene and 1 ml 10 wt% MAO). Polymer III was produced with the hafnocene (1.0g metalloocene and 3 ml 10 wt% MAO). Polymer IV was produced with Zirconocene 3 (1.0 mg metalloocene and 3 ml 10 wt% MAO).

Molecular weight (Mw and Mn) were measured by Gel Permeation Chromatography using a Waters 150 gel permeation chromatograph equipped with a differential refractive index (DRI) detector. The numerical analyses were performed using the commercially available standard Gel Permeation package, run on an HP1000 computer. The melting point of each polymer was measured by DSC and each was analyzed by carbon-13 NMR to determine stereoconfigurational distributions. The Carbon -13 NMR techniques used to measure stereoconfigurational percents and ratios are standard techniques disclosed in Polymer Sequence Determination;

The following properties were observed.
In Bovey's NMR nomenclature each "m" represents a "meso" dyad or successive methyl group on the same side of the polymer backbone and each "r" represents a "racemic" dyad or successive methyl group on alternative sides of the polymer backbone. Table 2 contains the carbon 13 NMR stereoconfigurational distributions for polymers I to IV.
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Percent solubility was measured by standard gravimetric method. For example, dissolving the polymer in decalin, filtering the solution, drying the residue in the filter and weighing the filter to determine the amount of polymer in the filter. This amount is reported as insoluble.

Both Polymer I and Polymer II were dissolved in decalin to the extent of two wt % at elevated temperature. The hot solution was then allowed to return to ambient temperature, i.e., about 18 degrees C. Neither polymer precipitated from solution at ambient temperature. Further, upon cooling the solution to 4 degrees C, both polymers remained in solution.

As is apparent from the foregoing description, the materials prepared and the procedures followed relate to specific preferred embodiments of the broad invention. It is apparent from the foregoing general description and the specific embodiments that, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of this invention.
Accordingly, it is not intended that the invention be limited thereby.
CLAIMS:

We Claim:

1. A composition, comprising:
   a syndiotactic polypropylene having a ratio
   of racemic mole fraction to meso mole fraction of about
   18:1 to about 1:1 dissolved in a liquid hydrocarbon at
   a temperature of 80 degrees Celsius or below.

2. The composition of claim 1 wherein the
   syndiotactic polypropylene has an Mw of about 400,000.

3. The composition of claim 1 or 2, wherein the
   liquid hydrocarbon is an aliphatic or aromatic
   hydrocarbon preferably decalin, xylene, hexane, decane,
   a petroleum resin, oil, wax or gasoline.

4. The composition of claim 1, 2 or 3, wherein
   the syndiotactic polypropylene is present in the
   solution at about 0.0001 wt.% or greater based upon the
   weight of the solution.

5. The composition of any of the above claims,
   wherein the ratio is about 12:1 to about 1:1.

6. The composition of any of the above claims,
   wherein the syndiotactic polypropylene has a ratio
   of racemic mole fraction to meso mole fraction of about
   12:1 to about 10:1 and a Mw of about 700,000, and the
   syndiotactic polypropylene is present in solution at a
   temperature of about 70 degrees Celsius or below and is
   present at about 0.5 weight percent or greater, based
   upon the weight of the solution and the syndiotactic
   polypropylene is at least about 80 percent soluble in
   the liquid hydrocarbon.

7. A process comprising:
dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon and forming an article by applying energy to the solution at 80 degrees Celsius or below.

8. A process comprising:
   dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon in an amount effective to reduce the viscosity of the hydrocarbon.

9. A process to graft syndiotactic polypropylene comprising:
   dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon with at least about 0.001 weight percent of a functional group under reaction conditions with an optional catalyst or initiator at about 70 degrees Celsius or below.

10. A process for solvent spinning syndiotactic polypropylene comprising:
    dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon, forcing the solution through a spinnerette at 80 degrees Celsius or below and optionally evaporating the solvent.

11. A coating or laminating process comprising:
dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon applying the solution to a substrate at 80 degrees Celsius or below and optionally evaporating the solvent.

12. a coating or a laminate process comprising:

dissolving at least about 0.05 weight percent of a syndiotactic polypropylene having a ratio of racemic mole fraction to meso mole fraction of about 18:1 to about 1:1 and a Mw of about 400,000 in a liquid hydrocarbon and forming an article by applying force or energy to the solution at 80 degrees Celsius or below.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 5 C08J3/09 D01F6/06

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)
IPC 5 C08J D01F

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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"A" document defining the general state of the art which is not considered to be of particular relevance
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"I" 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
‘X’ document of particular relevance; the claimed invention cannot be considered related to the invention
‘Y’ document of particular relevance; the claimed invention cannot be considered related to the invention
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Date of the actual completion of the international search 10 August 1994
Date of mailing of the international search report 02.09.94

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