

Description

The present invention relates to a process for the production of selectively hydrogenated polymers of conjugated dienes and more particularly to such a process utilizing a titanium hydrogenation catalyst.

The hydrogenation or selective hydrogenation of conjugated diene polymers has been accomplished using any of the several hydrogenation processes known in the prior art. For example the hydrogenation has been accomplished using methods such as those disclosed, for example, in U.S. Patent Nos. 3,494,942; 3,634,594; 3,670,054; 3,700,633 and Re. 27,145. These methods known in the prior art for hydrogenating polymers containing ethylenic unsaturation and for hydrogenating or selectively hydrogenating polymers containing aromatic and ethylenic unsaturation, involve the use of a suitable catalyst, particularly a catalyst or catalyst precursor comprising a Group VIII metal.

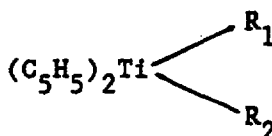
In the methods described in the foregoing patents, a catalyst is prepared by combining a Group VIII metal, particularly nickel or cobalt, compound with a suitable reducing agent such as an aluminum alkyl. Also, while aluminum alkyls are the preferred reducing agents, it is known in the prior art that alkyls and hydrides of metals of Groups I-A, II-A and III-B of the Periodic Table of the Elements are effective reducing agents, particularly lithium, magnesium and aluminum. In general, the Group VIII metal compound is combined with Group I-A, II-A or III-B metal alkyl or hydride at a concentration sufficient to provide Group I-A, II-A and/or III-B metal to Group VIII metal ratios within the range of from 0.1:1 to 20:1, preferably from 1:1 to 10:1. As indicated in the foregoing patents, the hydrogenation catalyst is generally prepared by combining the Group VIII metal compound and the reducing agent in a suitable solvent or diluent at a temperature within the range from 20 °C to 60 °C before the catalyst is fed to the hydrogenation reactor.

In 1985, Kishimoto et al. disclosed (in U.S. Patent 4,501,857) that selective hydrogenation of the unsaturated double bonds in conjugated diolefin polymers could be achieved by hydrogenating such polymers in the presence of at least one bis(cyclopentadienyl)titanium compound and at least one hydrocarbon lithium compound wherein the hydrocarbon lithium compound can be an added compound or a living polymer having a lithium atom in the polymer chain. European patent application 0,339,986 discloses that similar hydrogenation activity can be accomplished with the same titanium compounds in combination with an alkoxy lithium compound which can either be added directly or as a reaction mixture of an organo lithium compound with an alcoholic or phenolic compound. The use of these catalyst systems was said to be advantageous because the catalysts were said to be highly active so that they were effective even in such a small amount as not to affect adversely the stability of a hydrogenated polymer and require no deashing step. Further, the hydrogenation was said to be able to be carried out under mild conditions.

In U.S. Patent 4,673,714, bis(cyclopentadienyl)titanium compounds were disclosed which preferentially hydrogenate the unsaturated double bonds of conjugated diolefins but do not require the use of an alkyl lithium compound. These titanium compounds were bis(cyclopentadienyl)titanium diaryl compounds. The elimination of the need for the hydrocarbon lithium compound was said to be a significant advantage of the invention disclosed in the '714 patent.

The present invention provides a process for the preparation of hydrogenated conjugated diolefin polymers which comprises:

- a) terminating a living polymer obtained by polymerizing or copolymerizing at least a conjugated diolefin with an organo-alkali metal polymerization initiator, and preferably an organo lithium polymerization initiator, in a suitable solvent, by the addition of H₂, and
- b) selectively hydrogenating the unsaturated double bonds in the conjugated diolefin units of said terminated polymer by contacting the polymer, in the absence of hydrocarbon alkali metal and/or alkoxy alkali metal compounds, and preferably hydrocarbon lithium and alkoxy lithium, with hydrogen in the presence of at least one bis(cyclopentadienyl)titanium compound of the formula:



wherein R₁ and R₂ are the same or different and are selected from the group consisting of halogen groups, C₁-C₈ alkyl and alkoxy groups, C₆-C₈ aryloxy groups, aralkyl, cycloalkyl groups, silyl groups and carbonyl groups.

The living conjugated diolefin polymers which may conveniently be employed in the process of the present invention include conjugated diolefin homopolymers, copolymers of two or more conjugated

diolefins and of at least one conjugated diolefin and a second anionically polymerizable monomer, preferably being an alkenyl aromatic compound. Said conjugated diolefin polymers include random copolymers, block copolymers, tapered copolymers, which copolymers may be linear, branched or radial polymers. Block copolymers comprising at least two terminal alkenyl aromatic blocks and one intermediate conjugated diene block are a preferred class of block copolymers for use in the process of the present invention.

In general, when solution anionic techniques are used, conjugated diolefin polymers and copolymers of conjugated diolefins and alkenyl aromatic hydrocarbons are prepared by contacting the monomer or monomers to be polymerized simultaneously or sequentially with an anionic polymerization initiator such as Group IA metals, their alkyls, amides, silanates, naphthalides, biphenyls and anthracenyl derivatives. It is preferred to use an organoalkali metal (such as sodium or potassium) compound in a suitable solvent at a temperature within the range from -150°C to 300°C , preferably at a temperature within the range from 0°C to 100°C . Particularly effective anionic polymerization initiators are organolithium compounds having the general formula:



wherein:

R is an aliphatic, cycloaliphatic, aromatic or alkyl-substituted aromatic hydrocarbon radical having from 1 to 20 carbon atoms; and n is an integer of 1 to 4.

Conjugated diolefins which may be polymerized anionically include those conjugated diolefins containing from 4 to 12 carbon atoms such as 1,3-butadiene, isoprene, piperylene, methylpentadiene, phenylbutadiene, 3,4-dimethyl-1,3-hexadiene and 4,5-diethyl-1,3-octadiene. Conjugated diolefins containing from 4 to 8 carbon atoms are preferred for use in such polymers. Alkenyl aromatic hydrocarbons which may be copolymerized include vinyl aryl compounds such as styrene, various alkyl-substituted styrenes, alkoxy-substituted styrenes, 2-vinyl pyridine, 4-vinyl pyridine, vinyl naphthalene, alkyl-substituted and vinyl naphthalenes.

In general, any of the solvents known in the prior art to be useful in the preparation of such polymers may be used. Suitable solvents, then, include straight- and branched-chain hydrocarbons such as pentane, hexane, heptane and octane, as well as, alkyl-substituted derivatives thereof; cycloaliphatic hydrocarbons such as cyclopentane, cyclohexane and cycloheptane, as well as, alkyl-substituted derivatives thereof; aromatic and alkyl-substituted derivatives thereof; aromatic and alkyl-substituted aromatic hydrocarbons such as benzene, naphthalene, toluene and xylene; hydrogenated aromatic hydrocarbons such as tetralin and decalin; halogenated hydrocarbons, particularly halogenated aromatic hydrocarbons, such as chlorobenzene and chlorotoluene; linear and cyclic ethers such as methyl ether, methyl ethyl ether, diethyl ether and tetrahydrofuran.

Conjugated diolefin polymers and conjugated diolefin-alkenyl aromatic copolymers which may be used in the present invention include those copolymers described in U.S. Patents Nos. 3,135,716; 3,150,209; 3,496,154; 3,498,960; 4,145,298 and 4,238,202. Conjugated diolefin-alkenyl aromatic hydrocarbon copolymers which may be used in this invention also include block copolymers such as those described in U.S. Patent Nos. 3,231,635; 3,265,765 and 3,322,856. In general, linear and branched block copolymers which may be used in the present invention include those which may be represented by the general formula:



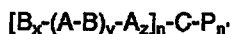
wherein:

A is a linear or branched polymeric block comprising predominantly monoalkenyl aromatic hydrocarbon monomer units;

B is a linear or branched polymeric block containing predominantly conjugated diolefin monomer units; x and z are, independently, a number equal to 0 or 1;

y is a whole number ranging from 0 to 15, and the sum of $x + z + y \geq 2$.

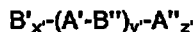
Polymers which may be treated in accordance with this invention also include coupled and radial block copolymers such as those described in U.S. Patent Nos. 4,033,888; 4,077,893; 4,141,847; 4,391,949 and 4,444,953. Coupled and radial block copolymers which may be treated in accordance with the present invention include those which may be represented by the general formula:



wherein:

A, B, x, y and z are as previously defined; n and n' are, independently, numbers from 1 to 100 such that $n + n' \geq 3$; C is the core of the coupled or radial polymer formed with a polyfunctional coupling agent; and

Each P is the same or a different polymer block or polymer segment having the general formula:



wherein:

A'' is a polymer block containing predominantly monoalkenyl aromatic hydrocarbon monomer units;

B' is a polymer block containing predominantly conjugated diolefin monomer units;

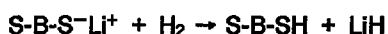
A'-B'' is a polymer block containing monoalkenyl aromatic hydrocarbon monomer units (A') and conjugated diolefin monomer units (B''), the A'-B'' monomer units may be random, tapered or block and when A'-B'' is block, the A' block may be the same or different from A'' and B'' may be the same or different from B';

x' and z' are, independently, numbers equal to 0 or 1; and

y' is a number from 0 to 15, with the proviso that the sum of $x' + y' + z' \geq 1$.

The radial polymers may, then, be symmetric or asymmetric.

In the production of the hydrogenated polymers of the present invention, the living polymers are terminated by utilizing hydrogen gas in place of the conventionally used alcohol terminating agent. The living polymer, or more accurately, the living end of the polymer chain, is terminated by the addition of hydrogen thereto. The theoretical termination reaction is shown using an S-B-S block copolymer for exemplary purposes:

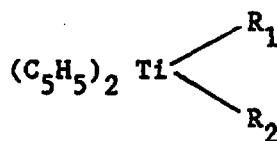


As shown above, it is theorized that lithium hydride is formed during the termination process. Formed in this manner, it is not a reactive polymerization initiator. It is inert to polymerization and does not interfere with the molecular weight control of the next polymerization batch as alcohol can.

It is usually advisable to contact and vigorously mix the hydrogen gas with the polymerization solution at the end of the polymerization reaction. This contact and vigorously mixing can be effected by adding the hydrogen gas through spargers in a mixing vessel containing polymer solution. The time of contact should be at least about ten seconds and preferably about twenty minutes to allow sufficient contact time for the reaction to occur. This is dependent upon the efficiency of the gas contacting equipment, gas solubility, solution viscosity and temperature. Alternatively, a continuous system could be employed whereby hydrogen is pumped into a solution prior to going to a statically mixed plug flow reactor. Hydrogen could also be dissolved in an appropriate solution and added to the polymer solution to be terminated. Another method would be to cause the hydrogen to be absorbed into an absorption bed and then cause the polymer solution to flow through the absorption bed. The hydrogen contact could also be carried out by adding a material which gives off hydrogen upon decomposition, i.e. diimide.

When this improvement is used, the problems of using alcohol, i.e. the formation of lithium alkoxides and excess alcohol impurities, are avoided. Furthermore, this process has been found to have significant advantage if the polymer made is to be hydrogenated. It has been found that if the present method is used, a bis(cyclopentadienyl)titanium hydrogenation catalyst can be used without the necessity of a hydrocarbon lithium or alkoxy lithium promoter, whether added with the catalyst or present in the living polymer.

As stated above, the hydrogenation step of the present process is carried out in the presence of a bis-(cyclopentadienyl)titanium compound of the formula:



wherein R_1 and R_2 are the same or different and are selected from the group consisting of halogen groups, C_1 - C_8 alkyl and alkoxy groups, C_6 - C_8 aryloxy groups, aralkyl, cycloalkyl groups, silyl groups and carbonyl groups. The hydrogenation step is carried out in the absence of hydrocarbon lithium and alkoxy lithium

compounds.

Specific bis(cyclopentadienyl) compounds which may be used in the present invention include bis-(cyclopentadienyl)titanium dichloride, bis(cyclopentadienyl)titanium dibromide, bis(cyclopentadienyl)titanium diiodide, bis(cyclopentadienyl)titanium difluoride, bis(cyclopentadienyl)titanium dicarbonyl, bis-
 5 bis(cyclopentadienyl)titanium dimethyl, bis(cyclopentadienyl)titanium diethyl, bis(cyclopentadienyl)titanium dibutyl (including n-butyl, sec-butyl, tert-butyl), bis(cyclopentadienyl)titanium bis(trimethylsilylmethyl), bis-(cyclopentadienyl)titanium dibenzyl, bis(cyclopentadienyl)titanium dihexyl, bis(cyclopentadienyl)titanium dimethoxide, bis(cyclopentadienyl)titanium diethoxide, bis(cyclopentadienyl)titanium dibutoxide, bis-
 10 bis(cyclopentadienyl)titanium dipentoxide, bis(cyclopentadienyl)titanium dineopentoxide, bis(cyclopentadienyl)titanium diphenoxide, and all mixtures thereof. The preferred titanium compound is bis(cyclopentadienyl)titanium dichloride because of ease of handling, air stability and commercial availability.

This process will selectively hydrogenate the double bonds of polymerized conjugated diolefins of a polymer as described hereinbefore, without hydrogenating alkenyl aromatic hydrocarbon units present therein to any degree. Hydrogenation percentages of greater than 50% are easily obtained but it has been
 15 found that in order to achieve hydrogenation percentages of greater than 95% as is often desired, the alkali metal (for example, lithium) to titanium ratio must be at least 2:1 and preferably is at least 6:1 and more preferably at least 10:1. There has to be sufficient alkali metal to ensure quick and sufficient interaction between the two metals. A high viscosity (high molecular weight) polymer may require a higher ratio because of the lesser mobility of the metals in the polymer cement. If alkali metal hydride is required to
 20 increase said alkali metal to titanium ratio, it can be made in situ by adding an organo alkali metal compound and hydrogen to the polymer (i.e., sparge), either before or after termination of the polymerization.

In general, the hydrogenation is carried out in a suitable solvent at a temperature within the range of from 0 ° to 120 °C, preferably from 60 to 90 °C, and at a hydrogen partial pressure within the range of
 25 from 0.069 bar (1 psig) to 82.8 bar (1200 psig), preferably from 6.9 bar (100 psig) to 13.8 bar (200 psig). Catalyst concentrations within the range of from 0.01 mM (millimoles) per 100 grams of polymer to 20 mM per 100 grams of polymer, preferably 0.04 to 1 mM catalyst per 100 grams of polymer, are generally used and contacting at hydrogenation conditions is generally continued for a period of time within the range of from 15 to 1440 minutes, preferably from 30 to 360 minutes. Suitable solvents for hydrogenation include,
 30 among others, n-heptane, n-pentane, tetrahydrofuran, cyclohexane, toluene, hexane and benzene. Because of the small amount of catalyst present in the polymer after hydrogenation, it is not necessary to separate the hydrogenation catalyst and catalyst residue from the polymer. However, if separation is desired, it may be carried out using methods well known in the prior art. Hydrogenation may be carried out in other manners such as batch processes, continuous processes, and semi-continuous processes.

35 The invention is further illustrated with the following examples for which the following information is provided.

Homopolybutadiene, polystyrene-polybutadiene-polystyrene, and polyisoprene-polystyrene block copolymers were terminated with hydrogen. Typically, at the end of the polymerization reaction, the living polymer cement was sparged with hydrogen gas (1.0 SCFM) from 5 to 60 minutes and vigorously mixed.
 40 Generally, the temperature of the polymer cement was 60 °C and no increase in temperature was observed during the termination step. During the sparging stage of the reaction, the total pressure in the reactor ranged from 2.76 bar (40 psig) to 6.9 bar (100 psig) of hydrogen. Termination was confirmed by four independent methods. The first of these was a simple colorimetric examination of the polymer cement. Styryllithium living ends have an absorption maximum at 328 mμ and thus have a distinct orange colour
 45 which turn colourless when the living ends are terminated. This was observed in hydrogen termination as samples were pulled from the reactor and visually, as well as colorimetrically, examined for colour change. The second method for determining termination was gel permeation chromatography (GPC). Analysis of the hydrogen terminated polymers by GPC showed that there was no high molecular weight polymer (HMP) formed. The absence of HMP generally indicates that the polymer has not crosslinked. Crosslinking is a
 50 typical detrimental side reaction in non-terminated polymer cements. Another method used to verify termination was ²H NMR. Deuterium gas was used to terminate the living polymer. During the termination, samples were submitted for ²H NMR analysis. Polymer termination was essentially complete when there was no increase in deuterium incorporation. The last method employed involved adding styrene monomer back to the terminated polymer. If any living ends are still existing after the sparge, they will polymerize the
 55 added monomer.

Example 1

A 272 kg (600 lb.) batch of polystyrene-polybutadiene-polystyrene (S-B-S⁻Li⁺) block copolymer 50,000 molecular weight was made by anionic polymerization using sec-butyllithium as the initiator in a 568 l (150 gallon) pressurized reactor. The polymerization took place in a mixture of cyclohexane and diethyl ether. The resulting polymer solution contained 20% polymer by weight.

At the end of the polymerization reaction, the reactor temperature was approximately 60 °C. The reactor was sparged with hydrogen for approximately 20 minutes. A colorimeter was used to determine when the termination was complete since S-B-S⁻Li⁺ has a distinct orange colour. The colorimeter reading still showed "colour" after 15 minutes of sparge time. At that time, the vent was closed and the reactor pressurized up to 5.5 bar (80 psig) with hydrogen. The temperature was raised to decrease viscosity and improve mass transfer. The solution was mixed for 20 more minutes. During that time, the colorimeter reading dropped to baseline which reflects a terminated polystyrene-polybutadiene-polystyrene (S-B-S) polymer.

All hydrogenation runs were carried out under similar conditions unless otherwise noted. A typical experimental hydrogenation run consisted of pressure transferring to a 4-litre reactor a 12-25% by weight solution of polymer. The temperature of the reactor was maintained at 70 °C. At this point, bis-(cyclopentadienyl)titaniumdichloride, (Cp₂TiCl₂), was added to the reactor as a toluene or cyclohexane slurry. After addition of the catalyst, the reactor was pressurized to 9.7 bar (140 psig) with hydrogen gas. The reaction was allowed to run for 3 hours, during which time samples were drawn from the reactor and analyzed by proton NMR to determine final percent conversion of olefin. Gel Permeation Chromatography (GPC) was done on final samples to determine if there had been any changes in molecular architecture.

Examples 2-7 [Hydrogenation of hydrogen terminated polymer with varying amounts of Cp₂TiCl₂ catalyst]

A polystyrene-polybutadiene-polystyrene type polymer of 50,000 molecular weight was prepared as in Example 1. The polymer solution was 20% by weight polymer. The polymer was hydrogenated with varying amounts of catalyst as indicated in Table 1. The results of the hydrogenation run are shown in Table 1.

Table 1

Example	Ti(mM) (100 gram polymer)	Li:Ti ratio	Olefin Conversion, %
2	0.04	56:1	97.2
3	0.08	28:1	98.5
4	0.16	14:1	99.6
5	0.48	5:1	99.3
6	0.80	3:1	98.5
7	2.24	1:1	87.5

Figure 1 graphically represents the Table 1 hydrogenation runs by showing percent olefin conversion over time. It was observed that catalyst loadings ranging from 0.04 to 0.80 mM Ti per 100 grams polymer resulted in >97% conversion of the olefin within 3 hours. As expected, the rate of hydrogenation decreased with decreasing catalyst loading, with the lowest catalyst loading of 0.04 mM Ti per 100 grams polymer requiring substantially longer reaction time. At a catalyst loading of 2.24 mM Ti per 100 grams polymer, it was observed that catalyst activity was initially incredibly rapid but leveled off quickly at only 87.5% conversion of the olefin. Noting this hydrogenation run, it appeared that there existed an optimum titanium concentration which was dependent on the concentration of LiH present from the polymerization termination step. Whereas the runs made with 0.04 to 0.80 mM Ti per 100 grams polymer always had an excess of LiH (Li:Ti ratios ranging from 56:1 to 3:1), the 2.24 mM Ti per 100 grams polymer run calculated to be a 1:1 Li:Ti ratio.

Example 8 [Hydrogenation of hydrogen terminated polymer with bis(cyclopentadienyl)titanium diethoxide]

A polystyrene-polybutadiene-polystyrene type polymer of 50,000 molecular weight was prepared as in Example 1. The polymer solution was 20% by weight polymer. Bis(cyclopentadienyl) titanium diethoxide (0.33 mM Ti per 100 grams polymer), as a cyclohexane slurry, was added to the reactor. After addition of the catalyst, the reactor was pressurized to 9.7 bar (140 psig) hydrogen and the temperature was

maintained at 70 °C. The hydrogenation reaction was allowed to proceed for 3 hours. Final conversion of the olefin was 98%.

Comparative Example A [Hydrogenation of methanol terminated polymer feed]

5

A 5% by weight solution of a polystyrene-polybutadiene-polystyrene type polymer of 50,000 molecular weight that had been terminated with methanol was transferred to a 4 litre reactor. The solution was sparged with hydrogen for 20 minutes. The contents of the reactor were heated to 40 °C and the hydrogen pressure within the reactor was 4.8 bar (70 psig). Bis(cyclopentadienyl)titanium dichloride (3.2 mM Ti per 100 grams of polymer) was added to the reactor as a catalyst/toluene slurry. During the first 150 minutes, no hydrogenation occurred. After 150 minutes, 7.5 mM of sec-butyl lithium was added and hydrogenation proceeded to 82% conversion.

Comparative Example B [Hydrogenation of methanol terminated polymer feed]

15

A 20% by weight solution of a polystyrene-polybutadiene-polystyrene type polymer of 50,000 molecular weight that had been terminated with methanol was transferred to a 4 litre reactor. The contents of the reactor were heated to 40 °C. The solution was sparged with hydrogen for 20 minutes. The reactor temperature was maintained at 70 °C and the hydrogen pressure within the reactor was 9.7 bar (140 psig). Bis(cyclopentadienyl)titanium dichloride (0.8 mM Ti per 100 grams of polymer) was added to the reactor as a catalyst/toluene slurry. During the first 120 minutes no hydrogenation occurred. After 120 minutes, 15 mM of sec-butyl lithium were added to the reactor and hydrogenation proceeded to 62% conversion.

Comparative Example C [Hydrogenation of a high molecular weight hydrogen terminated polymer]

25

A polystyrene-polybutadiene-polystyrene type polymer of 165,700 molecular weight was prepared as in Example 1. The polymer solution was 12.1% by weight polymer. The polymer was hydrogenated with bis-(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams polymer). The LiH:Ti ratio for the hydrogenation run was 4:1. The final conversion of the olefin was 10%. This LiH:Ti is not high enough for such a high molecular weight polymer.

Example 9 [Hydrogenation of a high molecular weight hydrogen terminated polymer]

To the polymer synthesized according to Example 1 was added 1.8 mM sec-butyl lithium, followed by sparging and vigorously mixing the polymer solution with hydrogen gas for 20 minutes. To ensure that all the sec-butyl lithium had reacted with the hydrogen gas, styrene monomer was added back to the polymer solution. The absence of orange colour (which would be present if sec-butyl lithium reacted with styrene) verified that there was only LiH present in the polymer solution. Next, bis(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams of polymer) was added to the polymer feed and the hydrogenation reaction was allowed to proceed. The LiH:Ti ratio for the hydrogenation run was 10:1. The final conversion of the olefin was 98.7%. Thus, by in situ generating additional LiH, the high molecular weight polymer can be successfully hydrogenated.

Example 10 [Hydrogenation of a high molecular weight hydrogen terminated polymer]

45

To the polymer synthesized according to Example 1 (12.1% solids) was added 1.8 mM sec-butyl lithium. The polymer solution was not sparged with hydrogen gas so more LiH is not formed. Next, bis-(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams polymer) was added to the polymer solution, and the hydrogenation reaction was allowed to proceed. The LiR:Ti ratio for the hydrogenation run was 6:1. The final conversion of the olefin was 14.3%.

Comparative Example D [Hydrogenation of a high molecular weight hydrogen terminated polymer]

To the polymer synthesized according to Example 1 (12.1% solids) was added a mixture of 1.8 mM sec-butyl lithium and 1.8 mM 2,6-di-*t*-butyl-4-methyl-phenol. The polymer was stirred for approximately three minutes. There was no hydrogen sparging so additional LiH was not formed. Next, bis-(cyclopentadienyl)titanium dichloride (0.16 mM per 100 grams polymer) was added to the polymer solution and the hydrogenation reaction was allowed to proceed. The LiOR:Ti ratio for the hydrogenation run was

6:1. The final conversion of the olefin was 0%.

Comparative Example E [Hydrogenation of a high molecular weight hydrogen terminated polymer]

To the polymer synthesized according to Example 1 (12.1% solids) was added 13 mM solid LiH - therefore, the LiH was not prepared in-situ. The polymer solution was sparged with hydrogen or nitrogen gas for 20 minutes. Next, bis(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams polymer) was added to the polymer solution and the hydrogenation reaction was allowed to proceed. The LiH:Ti ratio for the hydrogenation run was 43:1. The final conversion of the olefin was 0%.

Table 2 is a summary of five hydrogenation runs carried out on the higher molecular weight polymer prepared as above.

Table 2

Example	Ti (mM) (100 gram polymer)	LiH:Ti ratio	LiX:Ti ratio	Olefin Conversion, %
Comp. Ex. C	.16	4:1	-	10.0
9	.16	10:1	-	98.7
10	.16	4:1	6:1	14.3
Comp. Ex. D	.16	4:1	6:1	0.0
Comp. Ex. E	.16	4:1	39:1	0.0

Where X = R(butyl), OR(2,6-di-t-butyl phenoxide), or H.

Example 11 [Hydrogenation of hydrogen terminated high molecular weight polymer with additional LiH being generated in the Polymerization Reactor]

To a batch of living polystyrene-polybutadiene-polystyrene type block copolymer of 165,700 molecular weight was added sec-butyl lithium. The reactor temperature was approximately 60 °C. The reactor was then sparged with hydrogen for approximately 20 minutes to generate LiH by reaction of H₂ with sec-butyl lithium and also to terminate the polymerization. The resulting polymer solution contained 12.1% polymer by weight. The amount of LiH present in the polymer solution provides a LiH:Ti ratio of 10:1 for the hydrogenation reaction. The polymer solution was pressure transferred to a 4 litre reaction and heated to 70 °C. Bis(cyclopentadienyl)titanium dichloride (0.08 mM Ti per 100 grams of polymer) was then added to the polymer solution. The reactor was then pressurized to 9.7 bar (140 psig) with hydrogen. Within 120 minutes, the hydrogenation of the olefin proceeded to 99%. There was no evidence of polystyrene hydrogenation.

Example 12 [Hydrogenation of high molecular weight hydrogen terminated polymer with LiH prepared outside of hydrogenation reactor]

3.6 mM sec-butyl lithium was added to 20 grams of cyclohexane in a 100 mL pressure vessel. The pressure vessel was pressurized to 9.7 bar (140 psig) hydrogen and mixed for 10 minutes, thereby forming LiH. The solution was then added to a 20% by weight polymer solution of a 50,000 molecular weight polystyrene-polybutadiene-polystyrene polymer. The polymer solution with the added LiH was allowed to stir for approximately 20 minutes. The contents of the reactor were heated to 70 °C and pressurized to 9.7 bar (140 psig) with hydrogen gas. To the reactor was then added bis(cyclopentadienyl)titanium dichloride (0.08 mM Ti per 100 grams polymer) as a cyclohexane slurry. Within 150 minutes, the hydrogenation of the olefin proceeded to 96%. There was no evidence of polystyrene hydrogenation.

Example 13 [Hydrogenation of a hydrogen terminated polymer by a semi-continuous process]

A batch of hydrogen terminated polystyrene-polybutadiene-polystyrene type block copolymer of 50,000 molecular weight was evenly divided between two four litre reactors. To Reactor 1, no catalyst was added. To Reactor 2, bis(cyclopentadienyl)titanium dichloride (0.08 mM Ti per 100 grams of polymer) was added. Reactor 2 was then heated to 70 °C and pressurized to 9.7 bar (140 psig) with hydrogen gas. When the

appropriate temperature and pressure were attained, the polymer solution in Reactor 1 was fed into Reactor 2. The rate of addition of the polymer solution in Reactor 1 to Reactor 2 was 13 grams per minute. Total addition time of the polymer solution of Reactor 1 to Reactor 2 was one hour. At the end of the one hour reaction time, the conversion of olefin was 88%. The contents of the Reactor 2, now having all the polymer solution, were then left to stir at 70 °C and 9.7 bar (140 psig) of hydrogen for 1 hour more. At the end of this time the total olefin conversion was 98%.

Example 14 [Hydrogenation of hydrogen terminated polymer with catalyst and cocatalyst premixed]

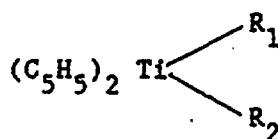
1.8 mM sec-butyl lithium was added to 50 grams of cyclohexane in a 100 mL pressure vessel. The pressure vessel was pressurized to 9.7 bar (140 psig) hydrogen and mixed for 5 minutes, thereby forming LiH. The solution was depressurized and bis(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams polymer) was added to the pressure vessel. The contents of the pressure vessel were then exposed to 9.7 bar (140 psig) hydrogen and mixed for 5 minutes. The catalyst solution was added to a 20% by weight solution of a polystyrene-polybutadiene-polystyrene type polymer of 165,700 molecular weight. The contents of the reactor were heated to 70 °C and pressurized to 9.7 bar (140 psig) hydrogen. Within 180 minutes, the hydrogenation proceeded to 98% conversion.

Example 15 [Hydrogenation of Hydrogen Terminated Polymer Containing Polyisoprene]

A 20% by weight solution of a polystyrene-polyisoprene-polystyrene type polymer of 100,000 molecular weight that had been hydrogen terminated was transferred to a 4-litre reactor. To the reactor was added 30 mM sec-butyl lithium. The solution was sparged with hydrogen for 30 minutes to convert all of the sec-butyl lithium to LiH. The contents of the reactor were heated to 90 °C and the hydrogen pressure within the reactor was 34.5 bar (500 psig). Bis(cyclopentadienyl)titanium dichloride (1.6 mM Ti per 100 grams of polymer) was added to the reactor as a catalyst/toluene slurry. Within 180 minutes, the hydrogenation proceeded to 77%. There was no evidence of polystyrene hydrogenation.

Claims

1. A process for the preparation of hydrogenated conjugated diolefin (co)polymers, which comprises:
 - (a) terminating a living polymer, obtained by polymerizing or copolymerizing at least a conjugated diolefin with an organo-alkali metal polymerization initiator in a suitable solvent, by the addition of hydrogen,
 - (b) selectively hydrogenating the unsaturated double bonds in the conjugated diolefin units of said terminated polymer by contacting the polymer, in the absence of hydrocarbon alkali metal and/or alkoxy alkali metal compounds, with hydrogen in the presence of at least one bis(cyclopentadienyl)-titanium compound of the formula



wherein R₁ and R₂ are the same or different and are selected from the group consisting of halogen, C₁-C₈ alkyl and alkoxy groups, C₆-C₈ aryloxy groups, aralkyl, cycloalkyl groups, silyl groups and carbonyl groups.

2. A process according to claim 1, characterized in that as polymerization initiator for the initial (co)-polymerization an organo lithium compound is used.
3. A process according to claim 1, characterized in that the selective hydrogenation step is carried out in the absence of hydrocarbon lithium and/or alkoxy lithium compounds.
4. A process according to claim 1, characterized in that the termination is carried out under contacting and vigorously mixing the polymerization solution at the end of the polymerization reaction.



appropriate temperature and pressure were attained, the polymer solution in Reactor 1 was fed into Reactor 2. The rate of addition of the polymer solution in Reactor 1 to Reactor 2 was 13 grams per minute. Total addition time of the polymer solution of Reactor 1 to Reactor 2 was one hour. At the end of the one hour reaction time, the conversion of olefin was 88%. The contents of the Reactor 2, now having all the polymer solution, were then left to stir at 70 °C and 9.7 bar (140 psig) of hydrogen for 1 hour more. At the end of this time the total olefin conversion was 98%.

Example 14 [Hydrogenation of hydrogen terminated polymer with catalyst and cocatalyst premixed]

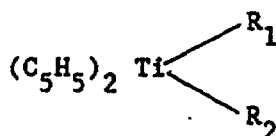
1.8 mM sec-butyl lithium was added to 50 grams of cyclohexane in a 100 mL pressure vessel. The pressure vessel was pressurized to 9.7 bar (140 psig) hydrogen and mixed for 5 minutes, thereby forming LiH. The solution was depressurized and bis(cyclopentadienyl)titanium dichloride (0.16 mM Ti per 100 grams polymer) was added to the pressure vessel. The contents of the pressure vessel were then exposed to 9.7 bar (140 psig) hydrogen and mixed for 5 minutes. The catalyst solution was added to a 20% by weight solution of a polystyrene-polybutadiene-polystyrene type polymer of 165,700 molecular weight. The contents of the reactor were heated to 70 °C and pressurized to 9.7 bar (140 psig) hydrogen. Within 180 minutes, the hydrogenation proceeded to 98% conversion.

Example 15 [Hydrogenation of Hydrogen Terminated Polymer Containing Polyisoprene]

A 20% by weight solution of a polystyrene-polyisoprene-polystyrene type polymer of 100,000 molecular weight that had been hydrogen terminated was transferred to a 4-litre reactor. To the reactor was added 30 mM sec-butyl lithium. The solution was sparged with hydrogen for 30 minutes to convert all of the sec-butyl lithium to LiH. The contents of the reactor were heated to 90 °C and the hydrogen pressure within the reactor was 34.5 bar (500 psig). Bis(cyclopentadienyl)titanium dichloride (1.6 mM Ti per 100 grams of polymer) was added to the reactor as a catalyst/toluene slurry. Within 180 minutes, the hydrogenation proceeded to 77%. There was no evidence of polystyrene hydrogenation.

Claims

1. A process for the preparation of hydrogenated conjugated diolefin (co)polymers, which comprises:
 - (a) terminating a living polymer, obtained by polymerizing or copolymerizing at least a conjugated diolefin with an organo-alkali metal polymerization initiator in a suitable solvent, by the addition of hydrogen,
 - (b) selectively hydrogenating the unsaturated double bonds in the conjugated diolefin units of said terminated polymer by contacting the polymer, in the absence of hydrocarbon alkali metal and/or alkoxy alkali metal compounds, with hydrogen in the presence of at least one bis(cyclopentadienyl)-titanium compound of the formula



wherein R₁ and R₂ are the same or different and are selected from the group consisting of halogen, C₁-C₈ alkyl and alkoxy groups, C₆-C₈ aryloxy groups, aralkyl, cycloalkyl groups, silyl groups and carbonyl groups.

2. A process according to claim 1, characterized in that as polymerization initiator for the initial (co)-polymerization an organo lithium compound is used.
3. A process according to claim 1, characterized in that the selective hydrogenation step is carried out in the absence of hydrocarbon lithium and/or alkoxy lithium compounds.
4. A process according to claim 1, characterized in that the termination is carried out under contacting and vigorously mixing the polymerization solution at the end of the polymerization reaction.



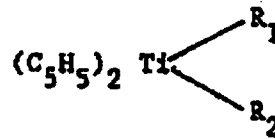
5. A process according to claim 4, characterized in that hydrogen is applied by sparging.
6. A process as claimed in claim 1, wherein the hydrogenation is carried out at a temperature in the range of from 0 °C to 120 °C and a pressure in the range from 0.069 bar (1 psig) to 83 bar (1200 psig) and the catalyst concentration is in the range of from 0.01 mM to 20 mM of titanium per 100 g of polymer and the contacting takes place for a period of time within the range of from 15 to 1440 minutes.
7. A process according to any of the claims 1-6, characterized in that the hydrogenation step is carried out in the presence of lithium hydride, formed in situ during the termination step of the living polymer.
8. A process as claimed in claims 1-7, wherein the alkali metal:titanium metal ratio during the hydrogenation is at least 2:1.
9. A process as claimed in claims 1-8, wherein additional alkali metal hydride is generated in situ by adding an organo-alkali metal compound and hydrogen to the polymer solution prior to addition of the hydrogenation catalyst.
10. A process as claimed in claims 1-9, wherein the hydrogenation is carried out at a temperature in the range of from 60-90 °C and a pressure in the range of from 6.9-13.8 bar (100-200 psig), the catalyst concentration is in the range of from 0.04-1.0 mM titanium per 100 g of polymer, the lithium hydride to titanium molar ratio is at least 6:1 and the contacting takes place for a period of time in the range of from 30 to 360 minutes.
11. A process as claimed in claims 1-10, wherein the molar ratio of lithium hydride to titanium is at least 10:1.
12. A process as claimed in any one of the preceding claims, wherein the alkali metal initiator to be used for initial polymerization is an organo lithium compound, and preferably sec-butyllithium.
13. A process as claimed in any one of the preceding claims, wherein the titanium compound is bis-(cyclopentadienyl)titanium dichloride.
14. A process as claimed in any one of the preceding claims, wherein the conjugated diolefin is selected from the group consisting of butadiene and isoprene.
15. A process as claimed in any one of the preceding claims, wherein the diolefin is copolymerized with a vinyl-substituted aromatic hydrocarbon.
16. A process as claimed in any one of the preceding claims, wherein the diolefin is copolymerized with a monomer selected from the group consisting of styrene and styrene derivatives.
17. A process as claimed in any one of the preceding claims wherein the copolymer is a block copolymer having at least one conjugated diene polymer block and at least one styrene or styrene derivative block.
18. A process as claimed in any one of the preceding claims, wherein at least 50% of the unsaturated bonds in the conjugated diene units are hydrogenated.
19. A process as claimed in any one of the preceding claims, wherein at least 95% of the unsaturated bonds in the conjugated diene units are hydrogenated.

Patentansprüche

1. Verfahren zur Herstellung von hydrierten, konjugierten Diolefin-(Co)polymeren mit folgenden Verfahrensschritten:
 - (a) Termination eines durch Polymerisation oder Copolymerisation von mindestens einem konjugierten Diolefin mit einem alkalimetallorganischen Polymerisationsinitiator in einem geeigneten Lösungsmittel erhaltenen lebenden Polymers durch Zusatz von Wasserstoff,



(b) selektive Hydrierung der ungesättigten Doppelbindungen in den konjugierten Diolefinheiten des terminierten Polymers durch Kontaktieren des Polymers mit Wasserstoff in Abwesenheit von Alkalimetall-Kohlenwasserstoff- und/oder Alkalimetall-Alkoxyverbindungen und in Gegenwart von mindestens einer Bis(cyclopentadienyl)titanverbindung der Formel:



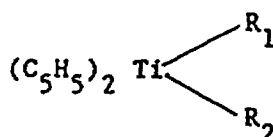
in der R_1 und R_2 gleich oder verschieden und aus der Gruppe bestehend aus Halogen-, C_1 - C_8 -Alkyl- und Alkoxygruppen, C_6 - C_8 -Aryloxygruppen, Aralkyl-, Cycloalkylgruppen, Silylgruppen und Carbonylgruppen ausgewählt sind.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man als Polymerisationsinitiator für die anfängliche (Co)polymerisation eine lithiumorganische Verbindung verwendet.
3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man den selektiven Hydrierungsschritt in Abwesenheit von Lithium-Kohlenwasserstoff- und/oder Lithium-Alkoxyverbindungen durchführt.
4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß man die Termination durch Kontaktieren unter kräftigem Vermischen der Polymerisationslösung am Ende der Polymerisationsreaktion durchführt.
5. Verfahren nach Anspruch 4, dadurch gekennzeichnet, daß man den Wasserstoff einbläst.
6. Verfahren nach Anspruch 1, wobei man die Hydrierung bei einer Temperatur im Bereich von 0°C bis 120°C und einem Druck im Bereich von 0,069 bar (1 psig) bis 83 bar (1200 psig) durchführt und wobei die Katalysatorkonzentration im Bereich von 0,01 mM bis 20 mM Titan je 100 Gramm des Polymers liegt und das Kontaktieren über einen Zeitraum von 15 bis 1440 Minuten stattfindet.
7. Verfahren nach einem der Ansprüche 1-6, dadurch gekennzeichnet, daß man den Hydrierungsschritt in Gegenwart von Lithiumhydrid, das während des Terminationsschritts des lebenden Polymers in situ gebildet wurde, durchführt.
8. Verfahren nach den Ansprüchen 1-7, wobei das Alkalimetall/Titan-Verhältnis während der Hydrierung mindestens 2:1 beträgt.
9. Verfahren nach den Ansprüchen 1-8, wobei durch Zusatz einer alkalimetallorganischen Verbindung und Wasserstoff zur Polymerlösung vor dem Zusatz des Hydrierkatalysators zusätzliches Alkalimetallhydrid in situ gebildet wird.
10. Verfahren nach den Ansprüchen 1-9, wobei man die Hydrierung bei einer Temperatur im Bereich von 60 - 80°C und einem Druck im Bereich von 6,9-13,8 bar (100-200 psig) durchführt, die Katalysatorkonzentration im Bereich von 0,04-1,0 mM Titan je 100 Gramm Polymer liegt, das molare Verhältnis von Lithiumhydrid zu Titan mindestens 6:1 beträgt und das Kontaktieren für einen Zeitraum von 30 bis 360 Minuten stattfindet.
11. Verfahren nach den Ansprüchen 1-10, wobei das Molverhältnis von Lithiumhydrid zu Titan mindestens 10:1 beträgt.
12. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich bei dem für die anfängliche Polymerisation zu verwendenden Alkalimetallinitiator um eine lithiumorganische Verbindung, vorzugsweise sec.-Butyllithium, handelt.

13. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich bei der Titanverbindung um Bis-(cyclopentadienyl)titanidchlorid handelt.
14. Verfahren nach einem der vorhergehenden Ansprüche, wobei man das konjugierte Diolefin aus der Gruppe, bestehend aus Butadien und Isopren, auswählt.
15. Verfahren nach einem der vorhergehenden Ansprüche, wobei man das Diolefin mit einem vinylsubstituierten aromatischen Kohlenwasserstoff copolymerisiert.
16. Verfahren nach einem der vorhergehenden Ansprüche, wobei man das Diolefin mit einem aus der Gruppe, bestehend aus Styrol und Styrolderivaten, ausgewählten Monomer copolymerisiert.
17. Verfahren nach einem der vorhergehenden Ansprüche, wobei es sich bei dem Copolymer um ein Blockcopolymer mit mindestens einem Polymerblock aus konjugierten Dienen und mindestens einem Styrol- oder Styrolderivatblock handelt.
18. Verfahren nach einem der vorhergehenden Ansprüche, wobei mindestens 50% der ungesättigten Bindungen in den konjugierten Dieneinheiten hydriert werden.
19. Verfahren nach einem der vorhergehenden Ansprüche, wobei mindestens 95% der ungesättigten Bindungen in den konjugierten Dieneinheiten hydriert werden.

Revendications

1. Un procédé pour la préparation de polymères ou copolymères hydrogénés de dioléfines conjuguées, qui comprend les étapes selon lesquelles :
- a) on termine un polymère vivant, obtenu par polymérisation ou copolymérisation d'au moins une dioléfine conjuguée avec un initiateur de polymérisation organométal alcalin dans un solvant approprié, par l'addition d'hydrogène,
- b) on hydrogène sélectivement les doubles liaisons insaturées dans les unités de dioléfines conjuguées de ce polymère terminé par mise en contact du polymère, en l'absence de composés hydrocarbure-métal alcalin et/ou alcoxy-métal alcalin, avec l'hydrogène en présence d'au moins un composé de bis(cyclopentadiényl)titan de la formule



dans laquelle R_1 et R_2 sont identiques ou différents et sont choisis dans le groupe constitué par les atomes d'halogènes, les groupes alcoyle et alcoxy en C_1 - C_8 , les groupes aryloxy en C_6 - C_8 , les groupes aralcoyle, cycloalcoyle, les groupes silyle et les groupes carbonyle.

2. Un procédé selon la revendication 1, caractérisé en ce que, comme initiateur de polymérisation pour la polymérisation ou copolymérisation initiale, on utilise un composé organolithien.
3. Un procédé selon la revendication 1, caractérisé en ce que l'étape d'hydrogénation sélective est conduite en l'absence de composés hydrocarbyllithium et/ou alcoyllithium.
4. Un procédé selon la revendication 1, caractérisé en ce que la terminaison est effectuée avec mise en contact et agitation énergétique de la solution de polymérisation à la fin de la réaction de polymérisation.
5. Un procédé selon la revendication 4, caractérisé en ce qu'on introduit l'hydrogène par barbotage.
6. Un procédé selon la revendication 1, dans lequel l'hydrogénation est effectuée à une température comprise entre 0°C et 120°C et à une pression comprise entre 0,069 bar et 83 bars et la concentration du catalyseur est comprise entre 0,01 mM et 20 mM de titane pour 100 g de polymère et



la mise en contact a lieu pendant un laps de temps compris entre 15 et 1440 minutes.

- 5 7. Un procédé selon l'une quelconque des revendications 1-6, caractérisé en ce que l'étape d'hydrogénation est conduite en présence d'hydruure de lithium, formé in situ durant l'étape de terminaison du polymère vivant.
8. Un procédé selon les revendications 1-7, dans lequel le rapport métal alcalin:titane durant l'hydrogénation est d'au moins 2:1.
- 10 9. Un procédé selon les revendications 1-8, dans lequel de l'hydruure de métal alcalin supplémentaire est produit in situ par addition d'un composé organo-métal alcalin et d'hydrogène à la solution de polymère avant l'addition du catalyseur d'hydrogénation.
- 15 10. Un procédé selon les revendications 1-9, dans lequel l'hydrogénation est effectuée à une température comprise entre 60 et 90 °C et une pression comprise entre 6,9 et 13,8 bars, la concentration du catalyseur est comprise entre 0,04 et 1,0 mM de titane pour 100 g de polymère, le rapport molaire de l'hydruure de lithium au titane est d'au moins 6:1 et la mise en contact a lieu pendant un laps de temps compris entre 30 et 360 minutes.
- 20 11. Un procédé selon les revendications 1-10, dans lequel le rapport molaire de l'hydruure de lithium au titane est d'au moins 10:1.
- 25 12. Un procédé selon l'une quelconque des revendications précédentes, dans lequel l'initiateur à base de métal alcalin à utiliser pour la polymérisation initiale est un composé organolithien, et de préférence le sec-butyllithium.
13. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le composé du titane est le dichlorure de bis(cyclopentadiényl)titane.
- 30 14. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la dioléfine conjuguée est choisie dans le groupe constitué par le butadiène et l'isoprène.
15. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la dioléfine est copolymérisée avec un hydrocarbure vinyl aromatique.
- 35 16. Un procédé selon l'une quelconque des revendications précédentes, dans lequel la dioléfine est copolymérisée avec un monomère choisi dans le groupe constitué par le styrène et les dérivés du styrène.
- 40 17. Un procédé selon l'une quelconque des revendications précédentes, dans lequel le copolymère est un copolymère séquencé ayant au moins un bloc de polymère de diène conjugué et au moins un bloc de styrène ou de dérivé du styrène.
- 45 18. Un procédé selon l'une quelconque des revendications précédentes, dans lequel au moins 50 % des liaisons insaturées des unités de diène conjugué sont hydrogénées.
- 50 19. Un procédé selon l'une quelconque des revendications précédentes, dans lequel au moins 95 % des liaisons insaturées dans les unités de diène conjugué sont hydrogénées.
- 55