

Description

This invention relates to a process and the sulfant composition whereby a lower alkene monomer is converted to a lower alkene polymer through the use of unique reaction conditions and catalyst system. The lower alkene polymers so obtained have a high degree of mono-unsaturation content and are highly reactive in various reactions.

It is known from United States Patent 2,816,944 issued December 17, 1957 to Muessig et al that olefinic polymers ranging in a carbon content of from 12 to 50 carbon atoms obtained from olefins having 5 to 25 carbon atoms may be prepared by using boron trifluoride with phosphoric acid. It is generally disclosed by Muessig et al that the polymerization may take place using kieselguhr, and is conveniently conducted at a temperature of 35°C to 60°C.

Serniuk in United States Patent 2,810,774 issued October 22, 1957 describes an olefin polymerization catalyst-system comprising boron trifluoride and acids of phosphorus. It is also disclosed by Serniuk that various absorbents such as aluminum silicates, kieselguhr, Fuller's earth, clays and silica gel may be employed as a support system for the catalyst. The Serniuk reference describes reaction temperatures of 77°F (24°C) to 212°F (100°C) during the polymerization. The olefins of Serniuk include a mixed propylene-butylene system having an active content of about 40% olefins.

United States Patent 2,976,338 issued March 21, 1961 to Thomas discloses a catalyst system comprising boron trifluoride and phosphoric acid as being too active for polymerizing olefins because of the rapid evolution of heat. It is disclosed that the boron trifluoride of Thomas may be modified through the inclusion of a potassium acid fluoride salt to give an acceptable product. The olefins employed by Thomas include from 5 to 15 carbon olefins for use in obtaining polymers containing from 10 to 30 carbon atoms. The reaction temperatures of the Thomas patent are generally in range of 32°F (0°C) to 212°F (100°C), preferably from 100°F (38°C) to 160°F (71°C).

It is known from the United States Patent 2,416,106 issued February 18, 1947 to Linn et al that olefins may be polymerized through the combination of boron fluoride and an acid fluoride metal. United States Patent 2,585,867 to Sparks et al issued February 12, 1952 describes the production of high molecular weight polymers from monomers using a boron trifluoride catalyst system with reaction temperatures from -40°C to -103°C. In particular, Sparks is concerned with the reaction of mono-olefins with di-olefins.

Blewett in United States patent 4,469,910 issued September 4, 1984 describes a process whereby a dimer fraction is reacted in an oligomerization process with an alpha-olefin in the presence of a phosphoric acid-modified boron tri-fluoride catalyst system. The Blewett reference is particularly concerned with the use of 6 to 12 carbon dimers obtained from the monomer which corresponds to the alpha-olefin. The oligomerization is conducted at from 5°C to 75°C. United States Patent 3,985,822 issued October 12, 1976 to Watson describes the production of poly-n-butenes using aluminum chloride as a catalyst and employing a reaction temperature of 65°F (18°C) to 115°F (46°C).

United States Patent 4,407,731 to Imai issued October 4, 1983 described catalytic compositions, useful in oligomerization and alkylation reactions, prepared by treating a metal oxide support such as aluminum with an aqueous solution of an acid. One of the catalysts suggested for use in the support system of Imai is boron fluoride. United States Patent 4,429,177 to Morganson et al issued January 31, 1984 describes obtaining an alpha-olefin polymer in the presence of a 3 component catalyst system comprising a solid absorbant, boron trifluoride and elemental oxygen. United States Patent 1,885,060 issued October 25, 1932 to Hofmann et al describes using boron fluoride as a catalyst for propylene or butylene. It is also disclosed that various hydrogen halides may also be utilized with the boron fluoride.

Schmurling et al United States Patent 2,369,691 issued February 20, 1945 describes the use of sulfuric acid and metal halides of the Friedel-Crafts type. The catalyst system is stated to be useful in the isomerization of saturated hydrocarbons, the alkylation of cyclic aliphatic hydrocarbons, and in the polymerization of unsaturated hydrocarbons. United States Patent 2,404,788 issued July 30, 1946 to Burk et al discloses various aluminate or silicate support systems for boron trifluoride.

United States Patent 4,400,565 issued to Darden et al August 23, 1983 describes oligomerizing olefins in the presence of boron trifluoride and a co-catalyst comprising a heterogeneous cationic ion exchange resin. United States Patent 2,442,645 to Elwell et al issued June 1, 1948 describes the polymerization of normal lower mono-olefins which are dissolved in liquid sulfur dioxide. The reaction according to Elwell is carried out in the presence of a boron fluoride catalyst.

United States Patent 2,406,869 to Upham issued September 3, 1946 describes the preparation of an olefin polymerization catalyst comprising boron trifluoride and a hydrogen halide source. United States Patent 2,199,180 to Laughlin which

issued April 30, 1940 describes the use of sulfuric acid and phosphoric acid for the polymerization of lower olefins. It is stated in Laughlin that it is desirable when treating the lower olefins to maintain the reaction temperature of above 200°F (95°C).

United States Patent 2,536,841 issued January 2, 1951 to Dornie describes the use of aluminum halides to polymerize olefins. The reaction temperatures suggested by Dornie are from 0°C to -164°C. Dornie utilizes a low-freezing non-reacting solvent such as chloroform or sulfur dioxide in his process. United States Patent 2,357,926 issued September 12, 1944 to Bannon describes the use of boron fluoride and water for the polymerization of olefins.

United States Patent 2,569,383 to Leyonmark et al issued September 25, 1951 describes the polymerization of olefins from mono-olefins and polyolefins to give drying oils. United States patent 2,960,552 to Wasley issued November 15, 1960 describes the use of methylchloride and boron trifluoride gas to polymerize lower olefins. United States Patent 2,855,447 issued October 7, 1958 to Griesinger et al describes an example of the polymerization of lower olefins through the use of hydrogen fluoride and boron trifluoride at temperatures of about 175°F (79°C). Bloch et al in United States Patent 3,126,420 issued March 24, 1964 describes the use of phosphoric acid and kieselguhr to polymerize propylene at temperatures of 450°F (232°C) to 650°F (343°C). The conditions for Bloch's reaction are from 600 to 1200 psi (4,100 KPa - 8,100 KPa). Griesinger in United States Patent 2,855,447 issued October 7, 1958 discloses that olefins may be polymerized with boron trifluoride.

Perilstein in United States Patent 3,749,560 issued July 31, 1973 describes the polymerization of a mixture of mono-olefins from C-12 and greater through the use of aluminum trichloride at temperatures of about 15°C to give polymers having a molecular weight of about 350 to about 1,500. Robert in United States Patent 3,932,553 issued January 13, 1976 discusses the polymerization of propylene in the presence of butadiene at 0°C to 60°C with boron trifluoride. Robert further discloses the use of phosphoric acid catalytic treatment of the di-olefin at from 130°C to 250°C. British patent 1,449,840 to Sanders published September 15, 1976 describes the alkylation of benzene through the use of a Friedel-Crafts catalyst system.

United States Patent 2,801,273 discloses a process for the production of polymers boiling in the gasoline range. Gaseous olefins are contacted at a temperature below about 100°C with a catalyst which comprises boron-fluoride and an or-

ganic compound with at least one active oxygen atom per molecule.

It has been found in the present invention that a high vinylidene content polymer may be obtained by reacting a lower alkene monomer in the presence of a boron trifluoride and mineral acid catalyst system at -3°C to -30°C thereby giving an olefin polymer which is useful for producing an oil soluble composition. The olefin polymers of the present invention are highly reactive materials in that they contain a large degree of reactive mono-unsaturation.

Throughout the specification and claims percentages and ratios are by weight, temperatures are in degrees Celsius, and pressures are in KPa gauge unless otherwise indicated. Ranges and ratios utilized herein are illustrative and such may be combined to further describe the invention. It is also understood that mixtures of ingredients may be employed for each stated ingredient. The references cited herein are, to the extent applicable, incorporated by reference for their disclosures.

The present invention describes a process for preparing a lower alkene polymer from a lower alkene monomer feed-stream, including the steps of: (A) contacting the lower alkene monomer with a catalyst system comprising boron trifluoride and at least one acid and (B) polymerizing the lower alkene monomer in the presence of the catalyst system at a temperature of -3°C to -30°C thereby obtaining a lower alkene polymer having a molecular weight of 250 to 500, the product of the process being a liquid at 20°C, the product of the process being a liquid at 20°C.

A further feature of the invention is a composition of matter which is a polymer of a C₂₋₆ mono-olefin having a molecular weight of 250, preferably at least 300, to 500 and a vinylidene to trisubstituted olefin content of at least 1:4, typically at least 1:3 and more typically at least 3:7 by weight, the C₂₋₆ mono-olefin preferably being propene.

Another feature of the invention is a composition of matter which is the polymer of a C₂₋₆ mono-olefin having the above-described molecular weight and a combined weight ratio of trisubstituted and tetrasubstituted olefin to the vinylidene of less than 9:1, typically less than 8:1, more typically less than 6:1 and most typically less than 4:1, preferably less than 17:2, the C₂₋₆ mono-olefin preferably being propene. Alternatively, the vinylidene to tetrasubstituted olefin weight ratio is at least 7:11.

Also described herein are various products including the lower alkene polymer, and the reaction product of the lower alkene polymer with an aromatic compound such as phenol, toluene or benzene and their sulfonated derivatives. Further de-

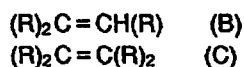
scribed herein are overbased compositions of the above sulfonated derivatives, preferably with a metal containing compound. The reaction products of the lower alkene polymer and a carboxylic acid acylating agent such as maleic acid or anhydride are also disclosed.

The present invention deals with the polymerization of lower alkene monomers to obtain a lower alkene polymer having a molecular weight of 250, preferably 300, to 500. The products obtained in the invention have a high degree of mono-unsaturation content typically at least 85 mole percent of the polymer, preferably at least 90% and even more preferably 95% - 100%.

The polymerization of the lower alkene monomer to the polymer desirably gives a product which contains a high vinylidene content. A vinylidene structure is as follows:



where each R group contains at least one carbon atom. As the various R groups become more complex, the later described alkylation process becomes more difficult. Moreover, the presence of a significant amount of trisubstituted olefin (B) or tetrasubstituted olefin (C), as shown below, significantly reduces the reactivity in alkylation reactions.



Thus, internal olefins are not as reactive in alkylation reactions as are vinylidene components.

In the present invention, the vinylidene content may be augmented by any alpha-olefin content present in the product or added to the product. An alpha-olefin is of the formula:



For convenience in defining the present invention, the following criteria is employed. The vinylidene content of the total mono-unsaturation present is typically at least 15%, more typically 20% and most typically at least 25%. The weight ratio of vinylidene to trisubstituted olefin is 1:4 to 8:1, typically 1:3 to 5:1, and often at least 1:4 and more typically at least 1:3. The amount of vinylidene and other substituted olefins are conveniently obtained by carbon 13 NMR as referred to in Determination of Molecular Structure of Hydrocarbon Olefins by High Resolution Nuclear Magnetic Resonance, Stehling et al, Anal. Chem. 38, (11), pp. 1467-1478 (1966). See also ¹³C Chemical Shifts of Some Model Olefins by Couperus et al, Org. Magn. Reson. 8, pp. 426-431 (1976).

In conjunction with the vinylidene content, it is preferred that the unsaturation content of the polymer is as defined as above and determined by ASTM D-1159-86 (Reapproved 1970) herein incorporated by reference.

The lower alkene polymer is obtained from a lower alkene monomer typically containing from 2 to 6 carbon atoms. Typically, the lower alkene monomer contains from 2 to 4 carbon atoms such as butene and most preferably propylene (propene).

The feed stream of the lower alkene monomer is preferably free of diene or higher moieties. The diene or higher unsaturated moieties can lead to the formation of diphenyl alkanes upon alkylation. By being substantially free of diene moieties, it is desired that there be no more than 10%, preferably no more than 5% by weight of diene or higher unsaturated moieties present in the feed stream. Most preferably, it is desired that the feed stream be completely free of diene moieties.

It is also highly desired that the alkene monomer such as the propylene or butene be an alpha olefin. By alpha olefin is meant that the unsaturation in the alkene monomer is between the first and second carbon atoms in the molecular structure. A further desired feature of the present invention is where the lower alkene monomer is at least 95% of a single species. By single species, it is meant that a single lower alkene monomer is the predominant species within the feed stream. That is, where the lower alkene monomer contains 4 carbon atoms, it is desirable that the monomer is substantially pure 1-butene rather than in a mixture with 2-butene or isobutylene. Of course, for the preferred propene only one isomer, e.g., 1-propene, exists.

The feed streams for the present invention are typically obtained through catalytic cracking of petroleum feed stocks. Thus, all of the lower alkene monomers with which the present invention is concerned are available as articles of commerce.

The lower alkene polymer obtained according to the present invention typically has a molecular weight between 250, preferably 300, and 500, preferably 325 to 475, more preferably from 350 to 450, and most preferably from 380 to 420. The lower alkene polymer, as later discussed, is conveniently utilized for the alkylation of benzene or other aromatic compounds which are then further converted to form alkylated aromatic sulfonic acids which are utilized as detergent substrates for overbasing in the lubricant industry. Other uses, as later described herein, are the alkylation of acylating agents such as carboxylic acids and anhydrides, and phenols.

The catalyst system employed herein has as a first component boron trifluoride. The boron trifluoride may be obtained as the gas commmer-

cially, generated in situ or obtained as the etherate.

The second component utilized as part of the catalytic system is a strong acid such as a mineral acid. The mineral acids include the hydrogen halides, sulfuric acid, sulfurous acid and the various phosphoric acids. Among the phosphoric acids are H_3PO_4 , HPO_3 and $\text{H}_4\text{P}_2\text{O}_7$. Any strong acid may be employed in the present invention provided that the desired polymer is obtained. Thus, while phosphoric acid or sulfuric acid are the preferred acids for use herein, any highly protic acid may be used. Thus, strong acid resins such as Amberlyst™ may be used in the present invention. The amount of acid is that amount sufficient to catalyze the reaction typically 0.005% to 1% by weight of the polymer.

It is also possible to superacidify the acids employed herein. Thus, it is possible to use oleum (fuming sulfuric acid) or glacial phosphoric acid through the introduction of P_2O_5 to phosphoric acid in order to increase the acid strength. It has been found, however, that the typical commercial strength acid, e.g., 85% phosphoric or 98% sulfuric are adequate within the present invention to accomplish the desired polymerization of the lower alkene monomer to the lower alkene polymer. Typically, a preferred acid is an aqueous solution containing 70–95% by weight of phosphoric acid (H_3PO_4).

The boron trifluoride is employed such that it saturates the reaction mixture. Due to the strength of both the acid and the corrosive nature of the source of boron trifluoride, it is suggested that the reactions be run in a glass lined or stainless steel vessel. Under the conditions with which the present invention is practiced, it is acceptable to run at atmospheric pressure.

It is believed that the restrictive temperature conditions under which the lower alkene monomer is polymerized in the presence of the catalyst system gives the high degree of unsaturation content retained in the polymer together with the narrow molecular weight distribution. In the present invention, it is highly desired that the product be mono-unsaturated so that it may be alkylated onto an aromatic ring in the desired manner. The subsequent alkylation conditions are such that internal unsaturation in a polymer of similar molecular weight but prepared outside the scope of the present invention will result in degradation of the polymer or products other than the desired alkylation products. Thus, temperature is viewed as being critical to the scope of the present invention in order to obtain the high vinylidene content with the desired 250 to 500 molecular weight. The temperature conditions under which the desired products of the present invention are obtained are from -3°C to -30°C , preferably -5°C to $-$

25°C and most preferably -8°C to -20°C . It was unexpected that the narrow temperature ranges within which the reaction is run in order to obtain the lower alkene polymer from the monomer would also result in a material which had a high reactive mono-unsaturation content of the desired molecular weight.

The catalyst system as previously discussed may be immobilized, heterogeneous, supported or in any other manner in which catalysts are utilized provided that the objects of the invention are met, preferably it is immobilized or supported. The substrates which may be employed in the present invention include Kieselguhr, clay, charcoal, aluminosilicates, alumina, silica, diatomaceous earth and various other metal silicates.

A heterogeneous catalyst system would, for example, simply be a mixture of BF_3 (boron trifluoride) and the acid, e.g., phosphoric. Typically, the heterogeneous system is obtained by bubbling gaseous boron trifluoride through the liquid acid/monomer/polymer mixture.

The temperature conditions of the present invention are met through the use of standard cooling devices. It is preferred that the polymerization of the lower alkene monomer to the lower alkene polymer be conducted such that the temperature of the reactants does not exceed the desired parameters for any substantial period of time during the processing. Thus, if a batch system is employed in order to obtain the lower alkene polymer, the reaction vessel and the contents should be maintained within the desired temperature range until substantially no lower alkene monomer is present, e.g., 5% or less. Where a continuous processing system is utilized, the lower alkene polymer is drawn off as it is formed.

Various solvents may be used in the present invention. It is conveniently preferred that a paraffinic hydrocarbon solvent which is normally liquid be employed herein. The solvent should be materials which are easily distillable from the reaction mixture following the polymerization reaction. Suitable examples of solvents include hexane, pentane, heptane, or butane. Other suitable solvents include halogenated aliphatics or carbon disulfide.

The following are examples of the present invention.

EXAMPLE I

A mixture is prepared comprising 200 grams hexane, 8 grams of phosphoric acid and 80 grams of DD1600 filter aid. The filter aid is utilized as the catalyst substrate. The premixture is obtained by first combining the filter aid and the hexane and thereafter adding 85% phosphoric acid to the

mixture. The mixture is stirred for about 30 seconds.

A 12-liter, 10-necked round bottom flask equipped with a stirrer, thermometer, dry ice/isopropanol condenser, 4 surface inlet tubes for propylene and 1 surface inlet tube for boron trifluoride is charged with the material described above. An additional 2200 grams of hexane solvent is added to the system.

The mixture described about is cooled to -20°C and boron trifluoride is introduced to the system at 1.0 cubic foot per hour (1.25 moles/hour) for 20 minutes until the system is saturated. Evidence of saturation will be observed by boron trifluoride fumes venting from the condenser. The rate of flow of the boron trifluoride is then adjusted to about 0.2 cubic foot per hour (0.25 mole/hour). The latter rate of boron trifluoride flow is maintained for the duration of the polymerization reaction.

Propylene gas is then added through the remaining 4 inlet tubes at 20 cubic feet per hour total (25 moles/hour). The temperature bath is maintained at -46°C to -60°C to hold the -20°C charge temperature. The flow rate of propylene is about 1 drop per minute condensed on a dry ice condenser during the propylene addition. A total of 121 cubic feet (150 moles) of propylene total is charged to the reaction vessel.

The propylene and boron trifluoride feed are stopped and the charge is neutralized with 80 grams of caustic soda liquid (50% aqueous). The charge is stirred for several hours to ensure neutralization. The product (lower alkene polymer) is filtered through a cake of approximately 30 grams of the DD1600 filter aid.

The product is then vacuum stripped in a separate 12-liter, 3-necked flask at 30 mm Hg (4 KPa) at 100°C to remove the hexane. A second strip at 9 mm Hg (1.2 KPa) at 163°C to remove the light ends results in the desired product in the amount of 5,418 grams.

The process will give near quantitative conversion to the polymer when a closed system is employed, e.g., the excess propylene is not vented.

EXAMPLE II

A 12-liter, 10-necked round bottom flask is equipped with a stirrer, thermometer, dry ice/isopropanol condenser, 4-surface inlet tubes for propylene and 1-surface inlet tube for boron trifluoride. The reaction vessel is immersed in a cooling bath and is charged with 2400 grams of hexane, 120 grams of silica gel and 12 grams of phosphoric acid in that order. The foregoing mixture is stirred at high speed for 15 minutes.

The reaction mixture is cooled to -27°C and boron trifluoride is added to the system at 1.5 cubic feet per hour (2.25 moles/hour) for a period of 23 minutes until the system is saturated. The boron trifluoride flow rate is then changed to 0.1 to 0.2 cubic feet per hour for the duration of the polymerization. The foregoing flow rate is sufficient to maintain saturation within the system.

Propylene is added through the remaining inlet tubes. The initial feed rate is 20 cubic feet per hour (30 moles/hour). In order to maintain the reaction mixture at -20°C , the flow rate of propylene is decreased by 20%. The bath temperature is maintained at -48°C to -50°C to maintain the -20° reaction temperature. The reaction is conducted over a period of about 5-1/2 hours at a rate of 1 drop of propylene per minute condensed on the dry ice condenser during the propylene addition. A total 98.3 cubic feet (148 moles) of propylene was charged to the reactor during the reaction time.

Following complete addition of the propylene, the boron trifluoride feed is stopped and the reaction mixture is neutralized with 200 grams of calcium hydroxide. The reaction mixture is stirred for several hours to ensure neutralization and the charge is filtered through 50 grams of DD1600.

The filtered reaction mixture is then placed in another reaction vessel and vacuum stripped at 100°C and 72mm mercury (9.5 KPa) to remove the hexane. Subsequently, the reaction mixture is raised to 161°C and a vacuum of 24 mm mercury (3.2 KPa) issued to remove 7 grams of light end material leaving a residue of 4,386 grams of the liquid product.

EXAMPLE III

A detergent alkylate is prepared from toluene and the lower alkene polymer of Example I.

Toluene in the amount of 4517 grams is added to a 12-liter 4-neck flask equipped with a stirrer, thermometer sub-surface tube and ice condenser. Thirty grams of aluminum chloride catalyst are also added to the flask.

The mixture described above is saturated with hydrogen chloride gas blowing through the sub-surface tube at 1 cubic foot (1.5 moles) per hour for 0.3 hours. The mixture at this point is cooled to -5°C .

The sub-surface tube is then replaced by an addition funnel and charged with 3000 grams of the polypropylene of Example I over a period of 1 hour. The reaction is exothermic and is maintained at a temperature between 0°C and 8°C . Following the complete addition of the polypropylene the reactants are stirred for an additional 3 hours. At this point, 61 grams of ammonium hydroxide are

slowly added through an addition funnel. Following complete addition of the ammonium hydroxide, the mixture is stirred for an additional 0.5 hours.

The reaction mixture is then filtered through 30 grams of DD1600 at 20°C. The filtrate is charged to a 12-liter, 4-necked flask equipped with a stirrer, thermometer, goose-neck and condenser receiver flask. The filtrate is then vacuum stripped to 160°C and 10 mm mercury (1.3 Kpa). The product is then allowed to cool to room temperature and filtered a second time through 30 grams of DD1600 to give 3505 grams of the filtrate as product.

The yield is approximately 95% wherein the product has an Mn by GPC of 402 and a Mw by GPC of 430. The viscosity at 100°C is 10.79 cks.

A further variation of the use of the composition of the present invention is the sulfonation of the above-described detergent alkylate according to conventional methods. A still further variation of the above example is to overbase the sulfonated detergent alkylate. Both of the foregoing techniques are known to one skilled in the art.

Claims

1. A process for preparing a lower alkene polymer from a lower alkene monomer feedstream, including the steps of: (A) contacting the lower alkene monomer with a catalyst system comprising boron trifluoride and at least one acid and (B) polymerizing the lower alkene monomer in the presence of the catalyst system at a temperature of -3°C to -30°C thereby obtaining a lower alkene polymer having a molecular weight of 250 to 500, the product of the process being a liquid at 20°C.
2. The process of claim 1 wherein the lower alkene is a C₂ - C₆ alkene monomer.
3. The process of claim 1 wherein the temperature is -5°C to -25°C.
4. The process of claim 1 wherein the lower alkene polymer has a molecular weight of 300 to 450.
5. The product obtained from the process of claim 1 which is alkylated onto an aromatic ring.
6. The product of claim 5 wherein the aromatic ring is sulfonated.
7. The product obtained from the process of claim 1 which is reacted onto a maleic acid or maleic anhydride.

8. A composition of matter comprising a polymer of a C₂-₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 having a molecular weight of 250 to 500 and a vinylidene to trisubstituted olefin content of at least 1:4 by weight.
9. A composition of matter which is a polymer of a C₂-₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 wherein the polymer has a molecular weight of 250 to 500 and a combined weight ratio of trisubstituted olefin and tetrasubstituted olefin to vinylidene of less than 9:1.
10. A composition of matter which is a polymer of a C₂-₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 wherein the polymer has a molecular weight of 250 to 500 and a vinylidene to trisubstituted olefin content of at least 3:7 by weight.

Patentansprüche

1. Verfahren zur Herstellung eines niederen Alken-Polymerisats aus einem Beschickungsstrom mit niederen Alken-Monomeren, das folgende Schritte einschließt:
(A) Zusammenbringen der niederen Alken-Monomere mit einem Katalysatorsystem, das Bortrifluorid und mindestens eine Säure enthält, und
(B) Polymerisation des niederen Alken-Monomers in Gegenwart des Katalysatorsystems bei einer Temperatur von -3°C bis -30°C, wobei ein niederes Alken-Polymerisat mit einem Molekulargewicht von 250 bis 500 anfällt und das Verfahrensprodukt bei 20°C eine Flüssigkeit ist.
2. Verfahren nach Anspruch 1, wobei das niedere Alken ein C₂ - C₆ - Alkenmonomer ist.
3. Verfahren nach Anspruch 1, wobei die Temperatur -5°C bis -25°C beträgt.
4. Verfahren nach Anspruch 1, wobei das niedere Alken-Polymerisat ein Molekulargewicht von 300 bis 450 hat.
5. Das Produkt, erhalten nach dem Verfahren von Anspruch 1, das an einen aromatischen Ring alkyliert ist.
6. Das Produkt nach Anspruch 5, wobei der aromatische Ring sulfoniert ist.



slowly added through an addition funnel. Following complete addition of the ammonium hydroxide, the mixture is stirred for an additional 0.5 hours.

The reaction mixture is then filtered through 30 grams of DD1600 at 20°C. The filtrate is charged to a 12-liter, 4-necked flask equipped with a stirrer, thermometer, goose-neck and condenser receiver flask. The filtrate is then vacuum stripped to 160°C and 10 mm mercury (1.3 Kpa). The product is then allowed to cool to room temperature and filtered a second time through 30 grams of DD1600 to give 3505 grams of the filtrate as product.

The yield is approximately 95% wherein the product has an Mn by GPC of 402 and a Mw by GPC of 430. The viscosity at 100°C is 10.79 cks.

A further variation of the use of the composition of the present invention is the sulfonation of the above-described detergent alkylate according to conventional methods. A still further variation of the above example is to overbase the sulfonated detergent alkylate. Both of the foregoing techniques are known to one skilled in the art.

Claims

1. A process for preparing a lower alkene polymer from a lower alkene monomer feedstream, including the steps of: (A) contacting the lower alkene monomer with a catalyst system comprising boron trifluoride and at least one acid and (B) polymerizing the lower alkene monomer in the presence of the catalyst system at a temperature of -3°C to -30°C thereby obtaining a lower alkene polymer having a molecular weight of 250 to 500, the product of the process being a liquid at 20°C.
2. The process of claim 1 wherein the lower alkene is a C₂-C₆ alkene monomer.
3. The process of claim 1 wherein the temperature is -5°C to -25°C.
4. The process of claim 1 wherein the lower alkene polymer has a molecular weight of 300 to 450.
5. The product obtained from the process of claim 1 which is alkylated onto an aromatic ring.
6. The product of claim 5 wherein the aromatic ring is sulfonated.
7. The product obtained from the process of claim 1 which is reacted onto a maleic acid or maleic anhydride.
8. A composition of matter comprising a polymer of a C₂-C₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 having a molecular weight of 250 to 500 and a vinylidene to trisubstituted olefin content of at least 1:4 by weight.
9. A composition of matter which is a polymer of a C₂-C₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 wherein the polymer has a molecular weight of 250 to 500 and a combined weight ratio of trisubstituted olefin and tetrasubstituted olefin to vinylidene of less than 9:1.
10. A composition of matter which is a polymer of a C₂-C₆ mono-olefin obtainable in a process according to anyone of the Claims 1 to 4 wherein the polymer has a molecular weight of 250 to 500 and a vinylidene to trisubstituted olefin content of at least 3:7 by weight.

Patentansprüche

1. Verfahren zur Herstellung eines niederen Alken-Polymerisats aus einem Beschickungsstrom mit niederen Alken-Monomeren, das folgende Schritte einschließt:
(A) Zusammenbringen der niederen Alken-Monomere mit einem Katalysatorsystem, das Bortrifluorid und mindestens eine Säure enthält, und
(B) Polymerisation des niederen Alken-Monomers in Gegenwart des Katalysatorsystems bei einer Temperatur von -3°C bis -30°C, wobei ein niederes Alken-Polymerisat mit einem Molekulargewicht von 250 bis 500 anfällt und das Verfahrensprodukt bei 20°C eine Flüssigkeit ist.
2. Verfahren nach Anspruch 1, wobei das niedere Alken ein C₂-C₆-Alkenmonomer ist.
3. Verfahren nach Anspruch 1, wobei die Temperatur -5°C bis -25°C beträgt.
4. Verfahren nach Anspruch 1, wobei das niedere Alken-Polymerisat ein Molekulargewicht von 300 bis 450 hat.
5. Das Produkt, erhalten nach dem Verfahren von Anspruch 1, das an einen aromatischen Ring alkyliert ist.
6. Das Produkt nach Anspruch 5, wobei der aromatische Ring sulfoniert ist.



7. Das Produkt nach Anspruch 1, das mit Maleinsäure oder Maleinsäureanhydrid umgesetzt ist.

8. Eine Zusammensetzung, enthaltend ein Polymerisat eines $C_2 - C_6$ -Monoolefins, erhältlich in einem Verfahren nach einem der Ansprüche 1 bis 4 mit einem Molekulargewicht von 250 bis 500 und einem Gewichtsverhältnis von Vinyliden- zu trisubstituiertem Olefingehalt von mindestens 1:4.

9. Eine Zusammensetzung, die ein Polymerisat eines $C_2 - C_6$ -Monoolefins ist, erhältlich in einem Verfahren nach einem der Ansprüche 1 bis 4, wobei das Polymerisat ein Molekulargewicht von 250 bis 500 hat und das vereinigte Gewichtsverhältnis von trisubstituiertem Olefin und tetrasubstituiertem Olefin zu Vinyliden weniger als 9:1 beträgt.

Eine Zusammensetzung, die ein Polymerisat eines $C_2 - C_6$ -Monoolefins ist, erhältlich in einem Verfahren nach einem der Ansprüche 1 bis 4, wobei das Polymerisat ein Molekulargewicht von 250 bis 500 hat und das Gewichtsverhältnis von Vinyliden- zu trisubstituiertem Olefingehalt mindestens 3:7 beträgt.

Revendications

1. Procédé de préparation d'un polymère d'alcène inférieur à partir d'un courant d'alimentation en alcène inférieur monomérique, comprenant les étapes consistant à : (A) mettre l'alcène inférieur monomérique en contact avec un système catalytique constitué de trifluorure de bore et d'au moins un acide et (B) polymériser l'alcène inférieur monomérique en présence du système catalytique, à une température qui fluctue de $-3^{\circ}C$ à $-30^{\circ}C$, de façon à obtenir ainsi un polymère d'alcène inférieur possédant un poids moléculaire d'environ 250 à environ 500, le produit du procédé étant un liquide à $20^{\circ}C$.

2. Composition suivant la revendication 1, caractérisée en ce que l'alcène inférieur est un alcène en $C_2 - C_6$ monomérique.

3. Procédé suivant la revendication 1, caractérisé en ce que la température fluctue de $-5^{\circ}C$ à $-25^{\circ}C$.

4. Procédé suivant la revendication 1, caractérisé en ce que le polymère d'alcène inférieur possède un poids moléculaire de 300 à 450.

5. Produit obtenu par mise en oeuvre du procédé selon la revendication 1, alkylé sur un noyau aromatique.

6. Produit suivant la revendication 5, caractérisé en ce que le noyau aromatique est sulfoné.

7. Produit obtenu par mise en oeuvre du procédé selon la revendication 1, ayant réagi avec l'acide maléique ou l'anhydride maléique.

8. Composition de matière comprenant un polymère d'une monooléfine en $C_2 - C_6$ pouvant être obtenu par un procédé selon l'une quelconque des revendications 1 à 4, possédant un poids moléculaire de 250 à 500 et une teneur en vinylidène à oléfine trisubstituée d'au moins 1:4 en poids.

9. Composition de matière qui est un polymère d'une monooléfine en C_2 à C_6 pouvant être obtenu par un procédé selon l'une quelconque des revendications 1 à 4, où le polymère possède un poids moléculaire de 250 à 500 et un rapport pondéral combiné d'oléfine trisubstituée et d'oléfine tétrasubstituée à vinylidène inférieur à 9:1.

10. Composition de matière qui est un polymère d'une monooléfine en C_2 à C_6 pouvant être obtenu par un procédé selon l'une quelconque des revendications 1 à 4, où le polymère possède un poids moléculaire de 250 à 500 et une teneur en vinylidène à oléfine trisubstituée d'au moins 3:7 en poids.