

POLYISOBUTYLENE PREPARED WITH LOW DILUENT CONTENT
REACTION MEDIUM

5 Cross-Reference to Related Application

 This application is based upon United States Provisional Application Serial No. 61/551,576, filed October 26, 2011, of the same title. The priority of Provisional Application Serial No. 61/551,576 is hereby claimed and its disclosure incorporated by reference into this application in its entirety

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Technical Field

 The present invention relates to the manufacture of polyisobutylene by way of cationic polymerization in a reaction medium with low diluent content, typically with high velocity as well as elevated circulation rates and turbulence in
15 a loop reactor operated with relatively high pressure drop across a recirculating pump.

Background of Invention

 Processes for cationically polymerizing olefins are known in the art.
20 United States Patent No. 6,858,690 to *Webb et al.* discloses a method of making butyl rubber wherein processing efficiency including heat transfer is improved by utilizing a tertiary halogen initiator. *See, also*, United States Patent No. 3,932,371 to *Powers* which discloses polymerization of copolymers of isoolefins and conjugated dienes in a two-phase system where propane is used as a diluent in
25 order to improve heat transfer.

 The polymerization of olefins using Friedel-Crafts type catalysts, such as boron trifluoride and aluminum trichloride is well known. The degree of polymerization of the products obtained varies according to which of the various
30 known polymerization techniques is used and also varies with the parameters used to control the reaction. The molecular weight of the polymeric product is directly

related to the degree of polymerization and that the degree of polymerization may be manipulated by manipulating process parameters so as to produce a variety of products having respective desired average molecular weights. Due to the nature and mechanics of the olefinic polymerization process, a polyolefin product has a single double bond remaining in each molecule at the end of the polymerization process. The position of this remaining double bond is often an important feature of the product. For example, polyisobutylene (PIB) molecules wherein the remaining double bond is in a terminal (vinylidene) position are known to be more reactive than PIB molecules wherein the remaining double bond is internal, that is, not in a terminal position. A PIB product wherein most of the double bonds are in a terminal position may often be referred to as high vinylidene or reactive PIB. The extent to which a polyolefin product has terminal double bonds may also be manipulated by manipulation of process parameters.

It is also known that alpha olefins, particularly PIB, may be manufactured in at least two different classes of material--regular and high vinylidene. Conventionally, these two product grades have been made by different processes, but both often and commonly use a diluted feedstock in which the isobutylene concentration may range from 40 to as high as 90% by weight. Non-reactive hydrocarbons, such as isobutane, n-butane and/or other lower alkanes commonly present in petroleum fractions, may also be included in the feedstock as diluents. The feedstock often may also contain small quantities of other unsaturated hydrocarbons such as 1-butene and 2-butene.

High vinylidene, or highly reactive PIB, a relatively new product in the marketplace, is characterized by a large percentage of terminal double bonds, typically greater than 70% and preferentially greater than 80%. This provides a more reactive product, compared to regular PIB, and hence this product is also referred to as highly reactive PIB. The terms highly reactive (HR-PIB) and high vinylidene (HV-PIB) are synonymous. The basic processes for producing HR-PIB all include a reactor system, employing BF_3 and/or modified BF_3 catalysts, such

that the reaction time can be closely controlled and the catalyst can be immediately neutralized once the desired product has been formed. Since formation of the terminal double bond is kinetically favored, short reactions times favor high vinylidene levels. The reaction is quenched, usually with an aqueous
5 base solution, such as, for example, NH_4OH , before significant isomerization to internal double bonds can take place. Molecular weights are relatively low. HR-PIB having an average molecular weight of about 950-1050 is the most common product. Conversions, based on isobutylene, are kept at 75-85%, since attempting to drive the reaction to higher conversions reduces the vinylidene
10 content through isomerization. Prior United States Patent No. 4,152,499 dated May 1, 1979, prior United States Patent No. 4,605,808 dated August 12, 1986, prior United States Patent No. 5,068,490 dated November 26, 1991, prior United States Patent No. 5,191,044 dated March 2, 1993, prior United States Patent No. 5,286,823 dated June 22, 1992, prior United States Patent No. 5,408,018 dated
15 April 18, 1995 and prior United States Patent No. 5,962,604 dated October 5, 1999 are all directed to related subject matter.

Other than the HR grades and the regular grades of PIB, a certain grade of PIB known as the enhanced grade has been more recently developed (EP 1381637
20 and related patents discussed below). The advantage of these series of products is that the overall reactivity is high without the need for high vinylidene content.

The present invention is directed, in part, to controlling the reaction in a loop reactor by lowering the diluent content and manipulating the tube velocity
25 and recirculation rate of the process fluid. The invention is particularly concerned with polymerization of isobutylene and includes significant improvements to existing technology in terms of diluent content, conversion, product attributes and so forth discussed in more detail below.

30 United States Patent No. 6,844,400 shows an apparatus for polymerizing isobutylene wherein the recirculation rate is specified in the range of 20:1 to 50:1

and notes that higher recirculation ratios increase the degree of mixing, leading to narrower polymer distributions. Col. 9, lines 37-59. The '400 patent teaches to use two reactors in order to increase the conversion and to use lower flow rates to increase the residence time. Col. 11, line 57 to Col. 12, line 11. Related patents
5 include United States Patent No. 6,777,506 and 6,858,188. These patents all teach to increase residence time in order to increase conversion and lower polydispersity. *See, also*, United States Patent No. 7,038,008 which discloses recirculation rates of 1000:1 to 1:1. *See* Col. 3, lines 55-64.

10 In United States Patent No. 7,645,847 it is noted a Reynolds Number of at least 2000 is desirable in a tube and shell reactor for making isobutylene. Col. 8, lines 26-36, as well as a recirculation rate of from 20:1 to 50:1, Col. 5, lines 54-64. Single reactor conversion rates are disclosed at 51% in Table 6 for a residence time of 58 seconds. The '847 patent mentions:

15 The molar ratio of BF_3 to complexing agent in the catalyst composition may generally be within the range of from approximately 0.5:1 to approximately 5:1, desirably within the range of from approximately 0.5:1 to approximately 2:1, and
20 preferably within the range of from approximately 0.5:1 to approximately 1:1. Ideally, the catalyst composition may simply be a 1:1 complex of BF_3 and methanol. In some preferred embodiments of the invention, the molar ratio of BF_3 to complexing agent in said complex may be approximately 0.75:1.
25 Col. 10, lines 14-23

and that:

30 Generally speaking, for PIB production the amount of the BF_3 catalyst introduced into the reaction zone should be within the range of from about 0.1 to about 10 millimoles for each mole of isobutylene introduced into the reaction zone. Preferably, the BF_3 catalyst may be introduced at a rate of about 0.5 to about 2 millimoles per mole of isobutylene introduced in the feedstock.
35 Col. 10, lines 36-43.

Conversion levels are conventionally inversely related to α -vinylidene content. Col. 14, lines 35-47. *See, also*, United States Patent No. 6,992,152 which notes temperatures of at least 0°C up to 60°F or higher. *Note* United States Patent No. 6,884,858, Example 2, where the reaction temperature is maintained at 90°F.

- 5 Process parameters appear in Table 4 of the '858 patent, Col. 15, including a Reynolds Number reported at 3180 and a recirculation rate of 50/1.7 or 29.4. Related patents include United States Patent Nos. 6,525,149; United States Patent Nos. 6,683,138; and 6,562,913.

- 10 The following patents describe mid-range vinylidene content polyisobutylene (PIB) polymers and processes for producing them: United States Patent Nos. 7,037,099; 7,091,285; 7,056,990; and 7,498,396. The products are characterized in that at least about 90% of the PIB molecules present in the product comprise alpha or beta position isomers. The vinylidene (alpha) isomer
15 content of the product may range from 20% to 70% thereof and the content of tetra-substituted internal double bonds is very low, preferably less than about 10% or 5% and ideally less than about 1-2%. The midrange vinylidene content PIB polymer products are prepared by a liquid phase polymerization process conducted in a loop reactor at a temperature of at least 60°F using a BF₃/methanol
20 catalyst complex and a contact time of no more than 4 minutes. Otherwise, processing is similar to the other patents noted above.

- Prior art systems are characterized by diluents content in the reaction mixture of 10 percent by weight or more and oftentimes by 50% by weight
25 diluents and more, requiring solvent recycle and/or involving high solvent costs. Likewise, prior art systems are typically characterized by linear velocity in reactor tubes of less than 10 ft/sec as is seen in European Patent No. EP 1 242 464. *Note* particularly Table 4 where a linear velocity of 9.3 ft/sec is specified as well as Tables 6 and 8 where linear velocities of 6.59 ft/sec appear.

Summary of Invention

Despite numerous advances in the art, there is a need to provide more energy efficient and higher yield processes which provide superior material having lower polydispersity, even when prepared with a lower solvent content
5 reaction mixture.

There is provided in one aspect of the invention a method of making a polyisobutylene polymer in a recirculating loop reactor with one or more reaction tubes in contact with a heat transfer medium. The process includes: (a) providing
10 a feed mixture consisting essentially of polymerizable monomer and catalyst to a residual reactor stream at a feed rate to form a reaction mixture, the reaction mixture containing less than 5% by weight diluent components; (b) recirculating the reaction mixture in the one or more reaction tubes of the loop reactor at a recirculation rate greater than the feed rate utilizing a recirculating pump
15 operating at a pressure differential, ΔP , corresponding to a recirculating flow; (c) polymerizing the reaction mixture in the one or more tubes of the loop reactor to convert the feed mixture to polyisobutylene polymer while cooling the one or more tubes of the loop reactor with the heat transfer medium; and (e) withdrawing polyisobutylene polymer from the loop reactor.

20 In connection with the inventive process, relatively low polydispersities can be maintained, even when low levels or even no diluent is used. *Note*, for example, Table 1, where molecular weight increases, while polydispersity and alpha vinylidene content remain relatively constant as the pressure drop and
25 velocity increase and the isobutane diluent level is reduced from 10 wt. % to about 3.5 wt.%. A low diluent process uses less material and is very desirable from an economic perspective as well as an environmental perspective, since solvent does not need to be recycled or disposed of. Reducing diluent(s) levels while maintaining desired product attributes is enabled by employing high velocity in
30 accordance with the invention. In a particularly preferred embodiment, the reaction mixture is without substantial levels of diluent. The effect is particularly

apparent in **Figure 1**, which is a plot of polydispersity (PDI) versus solvent concentration in the reaction medium for a highly reactive PIB product having a nominal number average molecular weight of 2400. It is seen in **Figure 1** that polydispersities remain at 2.2 or less even at zero solvent levels when high
5 circulation rates (corresponding to high pressure differentials across the pump) are employed versus polydispersities of almost 2.7 when lower circulation rates are used.

It was unexpectedly found that conversion increases with increased
10 recirculation rates at the same residence time, contrary to the teachings of the prior art. In this regard, *note Figure 2*, wherein it is seen that conversion dramatically increases from 65% or so up to more than 75% as the recirculation rate and tube velocity are increased. Higher yield is realized without significant additional capital or processing costs. It was also found that polydispersity decreases with
15 substantially the same residence time as circulation rates increase.

A still further unexpected result is that alpha content does not decrease with increasing conversion. The prior art also teaches away in this regard.

20 Conventional boron trifluoride catalyst systems reported in the patent literature typically produce somewhat less than 900 lbs PIB/lb of BF_3 and typically less than 450 lbs PIB/lb of BF_3 . Much higher production by catalyst is seen in accordance with the present invention; typically from 2 to 4 times more production per pound of BF_3 as discussed hereinafter in connection with the
25 following United States Patents: 7,485,764; 7,217,773; and 7,038,008. Catalyst usage decreases substantially as the linear velocity of the reaction mixture is increased. Lower fluoride use is also highly desirable in terms of cost reduction and environmental impact.

30 Still further features and advantages of the invention will become apparent from the discussion which follows.

Brief Description of Drawings

The invention is described in detail below with reference to the various Figures, wherein:

5 **Figure 1** is a plot of polydispersity versus diluents concentration in the reaction medium for highly reactive PIB product having a nominal number average molecular weight of 2400;

10 **Figure 2** is a plot of isobutylene conversion to polymer as a function of pressure differential across a recirculating pump in a loop reactor;

Figure 3 is a schematic diagram of a loop reactor of the class useful in practicing the present invention;

15 **Figure 4** lists equations useful for determining heat transfer and the overall heat transfer coefficient;

Figure 5 is a plot of catalyst feed as a function of pressure differential across a recirculating pump in a loop reactor; and
20

Figure 6 is a plot of methanol feed as a function of pressure differential across a recirculating pump in a loop reactor.

Detailed Description of Invention

25 The invention is described in detail below with reference to several embodiments and numerous examples. Such discussion is for purposes of illustration only. Modifications to examples within the spirit and scope of the present invention, set forth in the appended claims, will be readily apparent to one of skill in the art. Terminology used throughout the specification and claims
30 herein is given its ordinary meaning, for example, psi refers to pressure in lbs/inch² and so forth. Terminology is further defined below.

The improved process of the present invention features the use of a Friedel-Crafts catalyst which is complexed with a complexing agent. Many useful Friedel-Crafts catalysts are known to those of ordinary skill in the related art field. In particular, many useful catalysts are described in the patents referenced above.

5 Useful Friedel-Crafts catalysts include, for example, BF_3 , AlCl_3 , TiCl_4 , BCl_3 , SnCl_4 and FeCl_3 and the like. The complexing agent for the catalyst, and in particular for the BF_3 catalyst, may be any compound containing a lone pair of electrons, such as, for example, an alcohol, an ester or an amine. For purposes of the present invention, however, the complexing agent may be an alcohol,

10 desirably a primary alcohol, preferably a C1 -C8 primary alcohol (such as, for example, methanol, ethanol, propanol, isopropanol, hexyl alcohol and the like) and ideally methanol. The molar ratio of BF_3 to complexing agent in the catalyst composition is generally in the range of from approximately 0.5:1 to approximately 5:1 respectively, desirably within the range of from approximately

15 0.5:1 to approximately 2:1, and preferably within the range of from approximately 0.5:1 to approximately 1:1. Ideally, the catalyst composition may simply be a 1:1 complex of BF_3 and methanol as is seen in the examples. For purposes of convenience, "catalyst" refers to a Friedel-Crafts catalyst of the class described above, while "catalyst complex" refers to the Friedel-Crafts catalyst and

20 complexing agent up to a 1:1 molar ratio. When complexing agent is used in a molar excess with respect to the Friedel-Crafts catalyst it is referred to herein as modifier.

"Catalyst complex turnover number" and like terminology refers to the

25 weight of polymer produced per unit weight of catalyst complex employed in the process.

"Consisting essentially of" and like terminology refers to the recited components and excludes other ingredients which would substantially change the

30 basic and novel characteristics of the mixture or composition. Unless otherwise indicated or readily apparent, a composition or mixture consists essentially of the

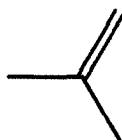
recited components when the composition or mixture includes 95% or more by weight of the recited components. That is, the terminology excludes more than 5% unrecited components.

5 Conversion of the reaction mixture to polymer is expressed in weight percent and calculated as the weight of polymer produced less the weight of isobutylene fed to the reaction system divided by the weight of isobutylene fed to the reaction system times 100%.

10 As used herein, “diluent”, “diluent” and like terminology refers to solvent components unreactive under reaction conditions and includes aliphatic hydrocarbon compounds such as butane, propane, hexane and so forth, specifically, for example, I-butane, n-butane, n-hexane and hexane isomers, as well as mixtures thereof. Diluents also include relatively unreactive alkenes such
15 as 1-butenes and the like which are present in the reaction mixture but do not polymerize under reaction conditions.

Polyisobutylene, “PIB” and like terminology refers to polymers made up of repeat units derived from isobutene, also referred to as isobutylene.

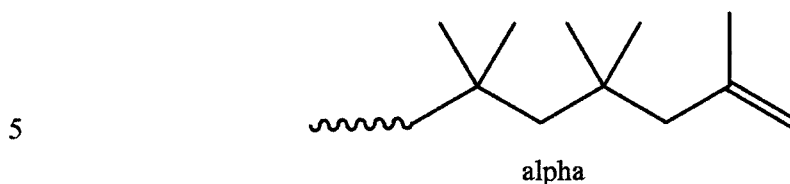
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isobutylene

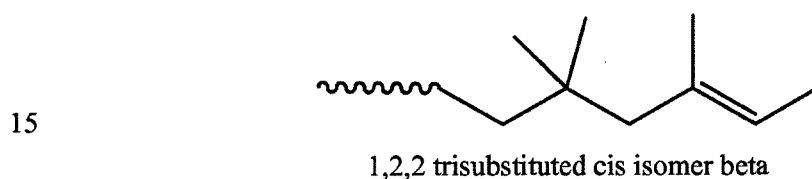
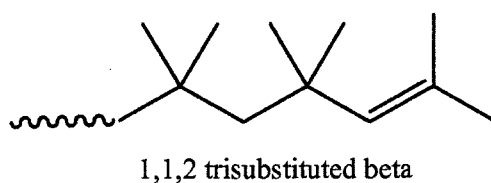
Such polymers are derived from feedstocks made up of purified isobutenes and hydrocarbon diluents, from isobutene concentrate, dehydro effluent, or from raffinate streams. The PIB polymer consists essentially of repeat units derived
25 from isobutylene, but may contain minor amounts of material derived from 1-butenes, butadiene or other C₄ olefins, 2-butenes (cis and/or trans) depending on the feedstock composition. Typically, the polymer is more than 99 % by weight derived from isobutylene monomer. Particular compositions of interest in

connection with the present invention have a number average molecular weight of from 500 to 4000 Daltons and in preferred embodiments significant amounts of alpha vinylidene terminated molecules:



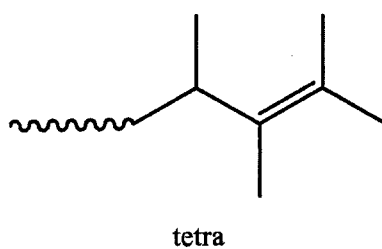
Highly reactive (HR) PIB polymer compositions typically include more than 80 mole % alpha molecules, while mid-range vinylidene content PIB products contain less alpha and more beta olefin isomers (1,1,2-trisubstituted or 1,2,2-

10 trisubstituted cis or trans isomer):

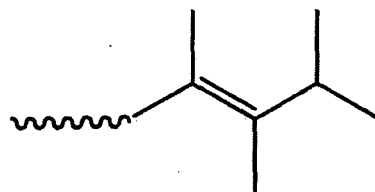


Other structures which may be present include tetrasubstituted structures, other trisubstituted structures with a double bond in the internal gamma position,

20 structures with other internal double bonds and aliphatic structures, for example:

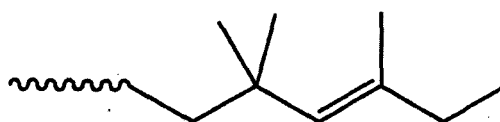


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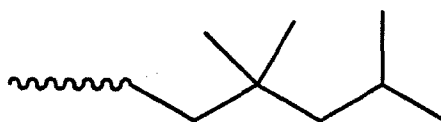
tetra

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gamma

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aliphatic

When calculating endgroup percentages, all PIB molecules found in the PIB compositions having a significant presence (more than half a percent or so) are included in endgroup calculations. The endgroup content is determined by nuclear magnetic resonance ^{13}C NMR as is well known in the art.

Suitable feedstocks include purified isobutenes with or without hydrocarbon diluents such as isobutane, hexane and so forth. Purified isobutene is readily available in bulk with purity levels of more than 95% by weight, for example 98.5% + by weight or 99.5% by weight in some cases. The purified isobutene may be fed with diluents as seen in the examples herein. Other suitable feedstocks include isobutene concentrate, dehydro effluent, or raffinate having relatively low levels of diluents.

One of skill in the art will appreciate that the feedstock may need to be purified to remove water and oxygenates such as alcohols, ethers and so forth to avoid adverse effects on the catalyst. Typical media for removal of impurities from hydrocarbon feed streams use molecular sieves, activated alumina and other hybrid adsorbents. A suitable absorbent to reduce water and oxygenate levels to desired limits is UOP AZ 300 (Des Plaines, IL, USA). Post treatment, prior to feeding to the reactor, the feed stream preferably has less than 3 ppm of oxygenates and less than 1 ppm of water.

A mid-range vinylidene polymer composition refers to a PIB wherein a first portion of the PIB molecules have alpha position double bonds and a second portion of the molecules have beta position double bonds, wherein said first and second portions together include at least 80 mole % of the PIB molecules of the composition, wherein said first portion includes less than 75 mole % of the PIB molecules of the composition, and wherein no more than 10 mole % of the PIB molecules of the composition have tetra-substituted double bonds, the first and second portions together includes at least 85 mole % of the PIB molecules of the composition and preferably the said first and second portions together include at least 90 mole % of the PIB molecules of the compositions. Typically, the first portion includes less than 72.5 mole % of the PIB molecules of the composition and sometimes less than 70 mole % of the PIB molecules of the composition. In preferred cases, no more than 5 mole % of the PIB molecules of the composition have tetra-substituted double bonds.

“Highly reactive PIB” and like terminology means polyisobutylene polymers with more than 80 mole percent alpha vinylidene terminated molecules.

Kinematic viscosity of the PIB products of the invention is expressed in Cst @100°C and is preferably measured in accordance with Test Method ASTM D 445.

Molecular weight herein is typically reported as number average molecular weight, in Daltons, and is measured by gel permeation chromatography (GPC). GPC measurements reported herein were carried out using a Viscotek GPCmax® instrument (Malvern instruments, Worcestershire, UK) employing a 3-column set-up (5µm (particle size) 100 Angstrom (pore size), 5µm 500Angstrom, 5µm 10⁴Angstrom) and a Refractive Index (RI) detector. Polyisobutylene standards were used to construct the calibration curve.

Polydispersity or PDI is defined as the ratio of the weight average molecular weight divided by the number average molecular weight of the polymer.

“Linear velocity” refers to the velocity of the recirculating reaction mixture in the tubes of the loop reactor and is calculated by dividing the volumetric flow rate of the reaction fluid by the cross-sectional area of the reaction tubes.

Recirculation ratio is calculated as the weight ratio of the reaction mixture recirculated to the feed added to the residual reactor stream.

Residence time is calculated as the volume of the reactor divided by the volumetric feed rate.

Any standard test method referred to herein is the version in effect as of January 1, 2011.

With the process of the invention, there are seen dramatic increases in conversion and improved product quality. Without being bound by any particular theory, it is believed that improved heat transfer and mixing, in part, provide the benefits observed. The heat transfer coefficient of the process fluid was increased by increasing the pressure differential across a recirculating pump thereby

increasing the velocity of the process fluid in the reactor tubes, likely decreasing the amount of relatively immobile material adjacent the reactor walls. In other words, by increasing the degree of turbulence of the tube side process fluid, the effect of undesirable boundary layer heat and mass transfer phenomena are reduced. The heat transfer is related to the Nusselt number of a fluid. Further, equations such as the Sieder Tate equations (for turbulent flow) provide a way to calculate the Nusselt number. These correlations relate the Nusselt number to the Reynolds number (ratio of inertial to viscous forces) and the Prandtl number (ratio of viscous diffusion to thermal diffusion). A potential problem faced in loop reactors is that there may be an increase in the viscosity of the tube side fluid at the heat transfer surface. This leads to a substantially lower internal heat transfer coefficient and a loss in conversion and productivity. It is seen in the examples which follow that the heat transfer coefficient increases dramatically and unexpectedly as the velocity in the tubes is increased above conventional levels.

15

EXAMPLES

Operation of the inventive process with a two-pass loop reactor is illustrated and described in connection in **Figure 3**. In **Figure 3** there is shown schematically a reactor system **10** which includes a two-pass loop reactor **12**, a recirculating pump **14** driven by a motor **16** with a variable speed drive **18**, a feed and recirculation loop indicated at **20** and a product outlet at **22**.

Reactor **12** includes a feed chamber **24**, a plurality of tubes indicated at **26** for upward flow, a plurality of tubes indicated at **28** for downward flow, as well as an upper plenum **30** and a receiving chamber **32** for circulated material. Reactor **12** is conventional in design and known in the art as a 1-2 shell and tube heat exchanger (1 shell, 2 pass). The reactor is suitably provided with 1164 tubes with tube outer diameter of 0.375" and a wall thickness of 0.035". The tubes are surrounded by a shell indicated at **34**, **36** for circulating chilled coolant since the polymerization reaction is highly exothermic.

30

In operation, isobutylene feedstock is fed to a residual reactor stream 38 via a feed line 40 to form a reaction mixture which is optionally provided with catalyst modifier, typically methanol, at an injection point at 42 just upstream of pump 14. Pump 14 operates at a pressure differential, ΔP , indicated in Figure 3 to recirculate the reaction mixture in reactor 12 via loop 20. A catalyst injection port at 44 provides a catalyst complex, for example one comprising a 1:1 molar mixture of methanol and BF_3 to the reaction mixture upstream of feed chamber 24.

Variable speed drive 18 contacts motor 16 which drives pump 14 at a pressure differential, ΔP , across the pump which, in turn, corresponds to a recirculating flow rate in the reactor for a reaction mixture. The flow characteristics of the reaction mixture are also influenced by temperature in the reactor, molecular weight, monomer and diluent content and so forth as is readily appreciated by one of skill in the art. The flow characteristics of the reaction mixture are thus controlled by feed and catalyst rates, conversion of monomer, mixture composition and the temperatures in the reactor as is seen in the examples which follow. For a given mixture, feed rates and temperature, recirculation rates and hence velocity of the reaction mixture in the tubes of the reactor is most conveniently controlled by controlling the speed of pump 14 to provide a pressure differential, ΔP (DP in the diagram), across the pump.

The pump circulates the reaction mixture to feed chamber 24 where the mixture is fed to a plurality of upwardly directed tubes indicated at 26 where it flows to plenum 30 before being transferred to a plurality of downwardly directed tubes indicated at 28 where it flows to receiving chamber 32. A polymerized product is withdrawn at 22 through a pressure relief valve indicated at 46. Residual reactor stream 38 remains in the system and feed line 40 provides fresh monomer to the residual stream as discussed above. Reactor 12 is operated under pressure sufficient to maintain the reaction mixture and its components in liquid form at reaction temperatures, suitably in the range of from about 40°F to about

90°F. Further details relating to the operation of reactor 12 are provided in European Patent 1 242 464, the disclosure of which is incorporated by reference.

Typically, the inventive process is operated wherein the recirculation rate is much higher than the feed rate as seen in the examples which follow. Coolant in the shell side of the reactor indicated at 34, 36, 48, 50 removes the heat of reaction. Any suitable coolant may be used, for example a 50:50 w/w mixture of water and methanol may be chilled and circulated in the shell section(s) to control reactor temperature.

10

Utilizing the procedure and materials described above, a 1-2 tube and shell reactor was operated to produce PIB using purified isobutylene diluted with isobutane and a BF_3 /methanol catalyst and modifier system. Details and results appear in Tables 1-3. In Tables 1-3, "catalyst complex" refers to a 1:1 w/w mixture of BF_3 /methanol. In these tables, the heat transfer coefficient, Q , is calculated from the log mean temperature difference as described immediately below and in connection with Equations (1)-(6) of Figure 4.

The heat transferred (Q) may be calculated either using shell-side (chilling fluid) or tube side (process fluid) data by Equation (1).

Q (BTU/hr) was calculated using tube reaction side data.

The terms in Equation (1) are as follows:

$\dot{m}_s$ = mass flow rate of shell side fluid (methanol-water);

c_{ps} = specific heat of the shell side (cooling) fluid;

25 t_1 = chiller temperature inlet;

t_2 = chiller temperature outlet;

$\dot{M}$ = mass flow rate of tube side fluid (process fluid)

c_{pT} = specific heat of the tube side fluid (process fluid)

T_1 = inlet temp of (reactor) process fluid;

30 T_2 = outlet temperature of (reactor) process fluid;

The Fourier Equation for heat transfer relates the overall heat transfer co-efficient; 'U' to the amount of heat transfer (Q). For a 1-2 heat exchanger (1 shell and 2 tube passes), the equation can be written in the form of Equation (2) and Equation (3). (Process heat transfer, D. Q. Kern, McGraw Hill, 1950, pg 144).

5

Δt of Equation (3) is also known as the log mean temperature difference (LMTD);

A = Area available for heat exchange

- 10 In Equation (4), F_t = fractional ratio of the true temperature difference to the LMTD.

For satisfactory operation of 1-2 heat exchangers, the value of F_t is generally desired to be greater than 0.75 (Process heat transfer, D. Q. Kern, McGraw Hill,

- 15 1950, pg 145). F_t can be calculated by Equations (4) and (5) or through figures relating the values of the dimensionless parameters R and S to F_t (Fig 18, pg 828, Kern, D.Q.).

- 20 R and S values for Equation 4 have been calculated in the Tables. F_t has been calculated from the R and S values.

The overall 'U' can be recalculated by rearranging equation (2) into the form shown in Equation (6).

- 25 The overall U as shown in equation (6) also appears in Tables 1-3.

Table 1 – Manufacture of Highly Reactive PIB, Nominal MN of 1000

Example	Delta Pressure, psi	Conversion, w/w%	Mn	PDI	KVIS-100°C, cST	Alpha-V	Isobutylene, wt %	Isobutane, wt %
1	25.00	65.37	1069	1.78	190	87	90.69	10.28
2	29.98	67.27	1056	1.80	191	86	90.54	10.40
3	30.00	66.73	1064	1.76	192	87	90.43	10.36
4	30.01	65.84			182		90.29	10.56
5	29.96	66.56	1050	1.77	184	86	90.38	10.48
6	34.98	67.48	1146	1.79		87	95.46	5.19
7	40.02	69.41	1091	1.78	178	88	95.72	5.24
8	50.04	70.77	1084	1.75	199	87	95.63	5.22
9	55.24	72.46	1083	1.76		87	97.09	3.81
10	54.75	71.37			194	87	96.42	3.73
11	55.21	72.50	1136	1.80	194	87	96.72	3.47
12	59.90	73.98					96.40	3.51
13	65.05	73.77	1090	1.76	210	87	96.32	3.51
14	64.99	74.94	1082	1.74	169	86	96.73	3.52
15	65.03	74.96			195		96.89	3.51
16	65.12	75.81	1087	1.74	194	85	97.14	3.58

Table 1 - Manufacture of Highly Reactive PIB, Nominal MN of 1000 (cont'd)

Example	Delta Pressure, psi	Feed rate, Gal / min	Catalyst Complex, ml/min	% change in catalyst	Methanol, ml/min	% change in methanol	Reactor temp. In, ° F	React temp Out, ° F
1	25.00	46.14	71.93	0.00	31.10	0.00	52.11	44.83
2	29.98	46.02	70.67	-1.76	31.14	0.12	52.03	45.27
3	30.00	46.00	70.39	-2.15	31.02	-0.26	52.02	45.27
4	30.01	46.08	70.77	-1.62	31.09	-0.04	52.00	45.35
5	29.96	45.95	70.25	-2.35	31.08	-0.06	52.18	45.38
6	34.98	44.89	71.15	-1.09	31.13	0.11	51.56	45.20
7	40.02	44.88	69.79	-2.99	30.91	-0.60	53.70	47.45
8	50.04	45.02	69.41	-3.51	31.14	0.13	53.62	47.78
9	55.24	46.22	70.94	-1.38	31.17	0.23	53.27	47.84
10	54.75	45.93	71.11	-1.15	31.03	-0.23	53.49	47.87
11	55.21	45.99	66.53	-7.52	27.85	-10.44	56.50	50.95
12	59.90	45.96	65.34	-9.16	28.29	-9.03	58.11	52.57
13	65.05	46.34	62.66	-12.89	25.74	-17.23	57.93	52.68
14	64.99	46.20	62.60	-12.98	25.81	-17.01	58.24	52.78
15	65.03	46.07	63.07	-12.32	26.20	-15.74	58.01	52.70
16	65.12	44.09	61.77	-14.14	25.94	-16.58	57.14	52.42

Table 1 - Manufacture of Highly Reactive PIB, Nominal MN of 1000 (cont'd)

Example	Delta Pressure, psi	Chiller Temp In, °F	Chiller Temp Out, °F	Chiller Flow, GPM	Recirc Flow, GPM	Recirc / Feed Ratio	Residence time, mins	PIB production rate, lbs / min
1	25.00	-6.76	-1.61	2000	1195	25.90	4.25	161
2	29.98	-7.02	-1.83	1999	1342	29.15	4.26	165
3	30.00	-6.89	-1.69	2000	1350	29.34	4.26	164
4	30.01	-8.75	-3.59	2000	1348	29.24	4.25	161
5	29.96	-8.80	-3.61	2000	1346	29.30	4.27	163
6	34.98	-7.56	-2.47	1999	1454	32.39	4.37	170
7	40.02	-6.91	-1.72	2000	1541	34.34	4.37	176
8	50.04	-6.58	-1.24	2000	1740	38.66	4.35	180
9	55.24	-4.89	0.64	1999	1851	40.06	4.24	192
10	54.75	-3.73	1.81	2000	1861	40.52	4.27	186
11	55.21	-3.78	1.77	2000	1831	39.82	4.26	190
12	59.90	-3.71	1.91	1999	1908	41.52	4.26	193
13	65.05	-3.53	2.18	2000	1986	42.86	4.23	194
14	64.99	-3.45	2.25	2000	1985	42.97	4.24	197
15	65.03	-2.88	2.80	2000	1986	43.10	4.25	197
16	65.12	-3.10	2.50	2000	1992	45.19	4.45	191

Table 1 - Manufacture of Highly Reactive PIB, Nominal MN of 1000 (cont'd)

Example	Delta Pressure, psi	Catalyst Complex rate, lbs / min	Turnover number, lbs PIB / lbs catalyst complex	Catalyst Efficiency, % improvement	Tube velocity, Ft/sec	Q, BTU/hr	LMTD	R
1	25.00	0.2220	726	0.00	9.01	-2459300	52.650	1.42
2	29.98	0.2181	757	4.31	10.1	-2783400	53.066	1.30
3	30.00	0.2172	753	3.72	10.1	-2803400	52.932	1.30
4	30.01	0.2184	739	1.82	10.1	-2780500	54.844	1.29
5	29.96	0.2168	751	3.49	10.1	-2796500	54.980	1.31
6	34.98	0.2196	776	6.90	11	-2956800	53.392	1.25
7	40.02	0.2154	816	12.36	11.6	-3200200	54.885	1.20
8	50.04	0.2142	838	15.46	13.2	-3717100	54.601	1.09
9	55.24	0.2190	875	20.54	14	-4091600	52.682	0.98
10	54.75	0.2195	849	16.90	14	-4121400	51.635	1.02
11	55.21	0.2053	925	27.48	13.8	-4066900	54.732	1.00
12	59.90	0.2017	958	31.91	14.4	-4285300	56.241	0.99
13	65.05	0.1934	1003	38.17	15	-4533700	55.979	0.92
14	64.99	0.1932	1021	40.68	15	-4524600	56.112	0.96
15	65.03	0.1947	1013	39.52	15	-4510900	55.394	0.94
16	65.12	0.1906	1004	38.25	15	-4461700	55.080	0.84

Table 1 - Manufacture of Highly Reactive PIB, Nominal MN of 1000 (cont'd)

Example	Delta Pressure, psi	S	F _t	U = Q/(A*delT_LMTD*F _t), Btu/(hr ft ² °F)	increase in ht coeff, %
1	25.00	0.087410	0.99774	42.68	0.00
2	29.98	0.087878	0.99791	47.91	12.27
3	30.00	0.088188	0.99791	48.38	13.37
4	30.01	0.084955	0.99809	46.30	8.50
5	29.96	0.085194	0.99805	46.46	8.86
6	34.98	0.086041	0.99810	50.58	18.52
7	40.02	0.085682	0.99820	53.25	24.77
8	50.04	0.088743	0.99825	62.17	45.67
9	55.24	0.095029	0.99819	70.92	66.19
10	54.75	0.096809	0.99805	72.90	70.82
11	55.21	0.092134	0.99828	67.85	58.99
12	59.90	0.090862	0.99835	69.57	63.02
13	65.05	0.092902	0.99840	73.94	73.27
14	64.99	0.092408	0.99835	73.62	72.52
15	65.03	0.093301	0.99835	74.35	74.23
16	65.12	0.092972	0.99854	73.95	73.28

A = 1097 sq. ft.

Table 2 – Manufacture of Mid-Range Vinylidene PIB, Nominal Mn of 3000 With Low Diluent

Example	Delta Pressure, psi	Conversion, w/w %	Mn	PDI	KVIS-100°C, cST	Alpha-V	Isobutylene, wt. %	Isobutane, wt. %
17	60.00	57.16					95.35	4.87
18	60.02	56.66	3127.00	2.27		64	95.14	5.01
19	60.00	56.66	3147.00	2.30		68	97.31	3.25
20	60.00	54.79					99.99	0.04
21	60.00	54.57					99.82	0.03
22	60.01	54.96					99.73	0.03
23	60.00	54.81					99.99	0.04
24	60.00	54.91	3132.00	2.33		69	99.99	0.04
25	60.00	55.10					99.76	0.04
26	60.01	55.30	3142.00	2.34		69	99.67	0.04

Table 2 – Manufacture of Mid-Range Vinylidene PIB, Nominal Mn of 3000 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Feed rate, Gal / min	Catalyst, complex ml/min	% change in catalyst	Methanol, ml/min	% change in methanol	Reactor temp In, ° F	React temp Out, ° F
17	60.00	54.99	30.86	0.00	0.00		44.50	40.24
18	60.02	55.00	31.34	1.53	0.00		43.48	39.22
19	60.00	55.01	32.36	4.85	0.00		43.47	39.17
20	60.00	54.99	33.51	8.56	0.00		43.97	39.60
21	60.00	54.99	32.70	5.94	0.00		44.02	39.60
22	60.01	53.00	31.85	3.20	0.00		42.96	38.65
23	60.00	51.00	30.52	-1.10	0.00		42.93	38.46
24	60.00	50.00	30.15	-2.30	0.00		44.02	39.55
25	60.00	49.99	29.98	-2.87	0.00		45.50	40.99
26	60.01	50.00	29.74	-3.63	0.00		45.50	40.97

Table 2 – Manufacture of Mid-Range Vinylidene PIB, Nominal Mn of 3000 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Chiller temp In, °F	Chiller Temp Out, °F	Chiller Flow, GPM	Recirc Flow, GPM	Recirc / Feed Ratio	Residence time, mins	PIB production rate, lbs / min
17	60.00	-13.09	-7.84	2000.10	2013.62	36.62	3.56	177
18	60.02	-13.08	-7.89	2000.22	2021.93	36.76	3.56	175
19	60.00	-13.00	-7.67	2000.13	2016.93	36.66	3.56	179
20	60.00	-12.84	-7.55	2000.01	1987.46	36.14	3.56	178
21	60.00	-13.09	-7.86	1999.97	1979.01	35.99	3.56	176
22	60.01	-13.61	-8.51	1999.96	1964.12	37.06	3.70	171
23	60.00	-13.74	-8.80	1999.99	1831.81	35.92	3.84	165
24	60.00	-13.36	-8.55	2000.02	1799.32	35.99	3.92	162
25	60.00	-15.18	-10.33	2000.01	1767.99	35.36	3.92	162
26	60.01	-15.43	-10.61	2000.09	1747.42	34.95	3.92	162

Table 2 – Manufacture of Mid-Range Vinylidene PIB, Nominal Mn of 3000 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Catalyst complex rate, lbs / min	Turnover number, lbs PIB / lbs catalyst complex	Catalyst Efficiency, % improvement	Tube velocity, Ft/sec	Q act, BTU/hr	LMTD	R
17	60.00	0.10	1853.73	0.00	13.60	-4228000	52.835	0.81
18	60.02	0.10	1805.97	-2.58	13.70	-4200900	51.834	0.82
19	60.00	0.10	1789.07	-3.49	13.70	-4303500	51.656	0.81
20	60.00	0.10	1716.52	-7.40	13.50	-4203500	51.980	0.83
21	60.00	0.10	1748.74	-5.66	13.40	-4138400	52.285	0.84
22	60.01	0.10	1740.93	-6.09	13.30	-4001500	51.861	0.85
23	60.00	0.09	1748.11	-5.70	12.40	-3613300	51.959	0.91
24	60.00	0.09	1737.79	-6.25	12.20	-3458500	52.737	0.93
25	60.00	0.09	1749.83	-5.61	12.00	-3426000	56.001	0.93
26	60.01	0.09	1768.67	-4.59	11.80	-3366700	56.256	0.94

Table 2 – Manufacture of Mid-Range Vinylidene PIB, Nominal Mn of 3000 With Low Diluent (cont'd)

Example	Delta Pressure, psi	S	F _t	$U = Q / (A \cdot \Delta T_{LMTD} \cdot F_t)$, Btu / (hr ft ² °F)	Change in ht coeff, %
17	60.00	0.091191	0.99866	73.04	0.00
18	60.02	0.091875	0.99862	73.98	1.28
19	60.00	0.094490	0.99856	76.05	4.12
20	60.00	0.093110	0.99857	73.82	1.06
21	60.00	0.091583	0.99859	72.25	-1.08
22	60.01	0.090081	0.99863	70.43	-3.58
23	60.00	0.087070	0.99863	63.48	-13.10
24	60.00	0.083790	0.99871	59.86	-18.05
25	60.00	0.079870	0.99883	55.83	-23.56
26	60.01	0.079085	0.99884	54.62	-25.23

A=1097 sq. ft.

Table 3 – Manufacture of Highly Reactive PIB, Nominal Mn of 2400 With Low Diluent

Example	Delta Pressure, psi	Conversion, w/w %	Mn	PDI	KVIS-100°C, cST	Alpha-V	Isobutylene, wt. %,	Isobutane, wt. %
27	60.01	57.44	2415.00	2.08	1664.42	86	96.55	3.56
28	59.98	57.63	2407.00	2.09	1707.70	86	96.69	3.30
29	60.00	56.78	2389.00	2.08	1667.07	85	98.31	2.15
30	60.02	56.73	2393.00	2.07	1645.59	86	98.29	2.09
31	60.00	56.43	2419.00	2.10	1689.38	85	99.20	0.55
32	59.98	56.51	2408.00	2.12	1710.58	86	99.22	0.58
33	60.02	56.68	2320.00	2.11	1551.14	85	99.99	0.03
34	59.99	56.28	2315.00	2.10	1533.73	85	99.98	0.03
35	60.02	56.79	2336.00	2.11	1566.38	86	99.77	0.03
36	59.99	56.85	2338.00	2.13	1617.92	86	99.66	0.03
37	59.98	56.22	2344.00	2.13	1597.41	86	99.99	0.03
38	60.01	56.49	2344.00	2.16	1633.07	85	99.67	0.03
39	60.01	56.64	2359.00	2.14	1632.77	85	99.65	0.03
40	60.00	56.65	2345.00	2.14	1597.79	86	99.67	0.03
41	60.00	56.67	2355.00	2.15	1618.27	86	99.64	0.03
42	60.00	56.34	2374.00	2.13	1639.80	85	99.99	0.03
43	60.00	56.26	2382.00	2.13	1651.53	85	99.76	0.03
44	60.01	57.10	2374.00	2.13	1626.18	86	99.80	0.03
45	59.99	56.46	2381.00	2.12	1594.45	86	99.99	0.03
46	60.01	56.42	2341.00	2.12	1602.48	85	99.99	0.03
47	60.01	56.89	2326.00	2.12	1579.76	85	99.94	0.03
48	60.00	56.68	2330.00	2.12	1579.03	86	99.89	0.03

Table 3 – Manufacture of Highly Reactive PIB, Nominal Mn of 2400 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Feed rate, Gal / min	Catalyst complex, ml/min	% change in catalyst	Methanol, ml/min	% change in methanol	Reactor temp In, ° F	React temp Out, ° F
27	60.01	52.96	68.30	0.00	22.02	0.00	30.00	25.21
28	59.98	52.99	68.26	-0.06	22.03	0.03	29.96	25.11
29	60.00	53.10	69.06	1.11	21.97	-0.22	31.00	26.17
30	60.02	52.99	68.89	0.86	21.98	-0.16	30.99	26.20
31	60.00	53.05	69.01	1.03	22.00	-0.08	31.00	26.17
32	59.98	52.99	68.74	0.63	22.05	0.15	30.99	26.13
33	60.02	53.01	72.77	6.55	23.97	8.85	32.00	27.05
34	59.99	53.05	72.89	6.72	24.04	9.16	31.95	27.14
35	60.02	53.03	72.17	5.66	24.03	9.15	31.52	26.56
36	59.99	52.94	72.09	5.55	24.04	9.17	31.00	26.10
37	59.98	53.00	72.49	6.13	23.91	8.61	31.00	26.16
38	60.01	52.94	72.19	5.69	23.97	8.87	30.96	26.09
39	60.01	53.02	72.22	5.74	23.99	8.95	30.96	26.13
40	60.00	53.01	71.95	5.34	24.17	9.77	31.03	26.15
41	60.00	52.92	71.78	5.09	23.98	8.92	31.00	26.12
42	60.00	52.99	72.19	5.69	23.94	8.74	30.98	26.14
43	60.00	52.97	71.93	5.31	23.98	8.93	31.04	26.11
44	60.01	53.03	71.65	4.91	23.93	8.69	31.53	26.65
45	59.99	52.99	72.40	6.00	23.93	8.68	31.51	26.69
46	60.01	53.05	72.34	5.91	23.96	8.79	31.52	26.70
47	60.01	53.01	72.42	6.03	24.07	9.30	31.45	26.65
48	60.00	52.96	72.12	5.60	24.07	9.31	31.49	26.62

Table 3 – Manufacture of Highly Reactive PIB, Nominal Mn of 2400 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Chiller temp In, °F	Chiller Temp Out, °F	Chiller Flow, GPM	Recirc Flow, GPM	Recirc / Feed Ratio	Residence time, mins	PIB production rate, lbs / min
27	60.01	-4.15	1.08	2000.36	2132.94	40.27	3.70	173
28	59.98	-4.54	0.63	1998.74	2128.58	40.17	3.70	174
29	60.00	-3.17	2.09	1999.18	2132.16	40.15	3.69	175
30	60.02	-2.61	2.52	2000.83	2136.98	40.33	3.70	174
31	60.00	-3.97	1.30	1999.56	2120.89	39.98	3.69	175
32	59.98	-4.28	0.88	1999.56	2116.98	39.95	3.70	175
33	60.02	-2.75	2.46	1998.41	2123.76	40.06	3.70	177
34	59.99	-2.45	2.78	1999.14	2126.52	40.08	3.69	176
35	60.02	-3.44	1.82	2000.56	2120.90	39.99	3.70	177
36	59.99	-3.87	1.29	2000.41	2120.52	40.05	3.70	177
37	59.98	-3.28	1.89	1999.45	2126.21	40.12	3.70	176
38	60.01	-3.25	1.88	2000.21	2126.77	40.18	3.70	176
39	60.01	-3.95	1.24	1999.62	2119.66	39.98	3.70	176
40	60.00	-4.14	1.09	2000.18	2118.62	39.97	3.70	176
41	60.00	-4.81	0.44	1999.60	2112.20	39.91	3.70	176
42	60.00	-3.29	1.91	2000.44	2126.54	40.13	3.70	176
43	60.00	-3.94	1.23	2000.79	2119.81	40.02	3.70	175
44	60.01	-4.25	0.98	1999.51	2112.78	39.84	3.70	178
45	59.99	-3.12	2.15	1998.99	2124.48	40.09	3.70	176
46	60.01	-2.59	2.67	1999.80	2129.07	40.14	3.69	176
47	60.01	-3.44	1.77	2000.00	2120.00	39.99	3.70	178
48	60.00	-3.89	1.34	1999.37	2116.45	39.96	3.70	177

Table 3 – Manufacture of Highly Reactive PIB, Nominal Mn of 2400 With Low Diluent (cont'd)

Example	Delta Pressure, psi	Catalyst complex rate, lbs / min	Turnover number, lbs PIB / lbs catalyst complex	Catalyst Efficiency, % improvement	Tube velocity, Ft/sec	Q act, BTU/hr	LMTD	R
27	60.01	0.21	820.93	0.00	14.40	-4458000	29.141	0.92
28	59.98	0.21	825.78	0.59	14.40	-4404200	29.489	0.94
29	60.00	0.21	819.34	-0.19	14.40	-4482500	29.123	0.92
30	60.02	0.21	818.86	-0.25	14.50	-4383300	28.642	0.94
31	60.00	0.21	821.46	0.06	14.40	-4465700	29.918	0.92
32	59.98	0.21	825.07	0.50	14.30	-4373000	30.258	0.94
33	60.02	0.22	788.10	-4.00	14.40	-4424100	29.669	0.95
34	59.99	0.22	781.84	-4.76	14.40	-4446100	29.372	0.92
35	60.02	0.22	794.84	-3.18	14.40	-4459500	29.852	0.94
36	59.99	0.22	794.33	-3.24	14.40	-4377400	29.839	0.95
37	59.98	0.22	784.57	-4.43		-4394900	29.271	0.93
38	60.01	0.22	788.22	-3.98		-4364700	29.212	0.95
39	60.01	0.22	791.00	-3.65		-4399500	29.901	0.93
40	60.00	0.22	794.21	-3.26		-4431700	30.109	0.93
41	60.00	0.22	794.70	-3.20		-4427200	30.744	0.93
42	60.00	0.22	789.38	-3.84		-4421600	29.242	0.93
43	60.00	0.22	788.99	-3.89		-4379200	29.930	0.95
44	60.01	0.22	805.15	-1.92		-4416800	30.727	0.93
45	59.99	0.22	788.78	-3.92		-4477200	29.584	0.91
46	60.01	0.22	789.69	-3.81		-4479900	29.073	0.92
47	60.01	0.22	794.56	-3.21		-4414400	29.883	0.92
48	60.00	0.22	793.60	-3.33		-4426400	30.326	0.93

Table 3 – Manufacture of Highly Reactive PIB, Nominal Mn of 2400 With Low Diluent (cont'd)

Example	Delta Pressure, psi	S	F _t	U = Q/(A*delT_LMTD*F _t), Btu/ (hr ft ² F)	increase in ht coeff, %
27	60.01	0.15308	0.99507	140.14	0.00
28	59.98	0.15000	0.99517	136.80	-2.38
29	60.00	0.15388	0.99498	141.01	0.62
30	60.02	0.15265	0.99498	140.21	0.05
31	60.00	0.15060	0.99524	136.71	-2.45
32	59.98	0.14648	0.99541	132.35	-5.56
33	60.02	0.14993	0.99509	136.60	-2.53
34	59.99	0.15204	0.99511	138.66	-1.06
35	60.02	0.15042	0.99510	136.85	-2.35
36	59.99	0.14806	0.99524	134.37	-4.12
37	59.98	0.15084	0.99512	137.54	-1.86
38	60.01	0.15003	0.99510	136.87	-2.33
39	60.01	0.14868	0.99530	134.76	-3.84
40	60.00	0.14877	0.99528	134.81	-3.81
41	60.00	0.14640	0.99547	131.86	-5.91
42	60.00	0.15177	0.99507	138.51	-1.16
43	60.00	0.14772	0.99524	134.01	-4.37
44	60.01	0.14611	0.99547	131.63	-6.08
45	59.99	0.15222	0.99515	138.63	-1.08
46	60.01	0.15426	0.99497	141.17	0.73
47	60.01	0.14927	0.99531	135.29	-3.46
48	60.00	0.14784	0.99535	133.67	-4.61

A=1097 sq. ft.

The various features and advantages of the invention are readily apparent from Tables 1-3 and the appended Figures. Table 1 provides results for high vinylidene, HR PIB having a number average molecular weight of about 1000. It is seen in **Figure 2** that conversion increases dramatically as the pressure differential, delta P, across the recirculating pump increases along with the linear velocity of the reaction mixture within the tubes of the reactor. Catalyst productivity also increases dramatically throughout the foregoing examples as pressure differential and linear velocity is increased. *Note Figure 5* where this aspect is illustrated. When making HR PIB, it is seen modifier consumption is reduced at high circulation rates, while conversion is increased; *see Figure 6*.

Following the procedures noted above in connection with **Figure 3** and Tables 1-3, there is provided in Table 4 a comparison of an HR-PIB product having a nominal number average molecular weight of 2400 made at different circulation rates and velocities, that is, made at different pressure differentials, DP, across a recirculation pump. It is seen in the data, shown graphically in **Figure 1**, that polydispersities remain below 2.2 even at zero solvent levels when high circulation rates (corresponding to high pressure differentials across a recirculating pump) are employed versus polydispersities of almost 2.7 when lower circulation rates are used. Lower polydispersities are especially desirable when the products are used for making derivatives such as alkyl phenols and/or fuel additives or lubricating oil additives. Lower polydispersities are associated with lower engine deposits in connection with fuel additives. Mid range vinylidene products also produce fewer byproducts when derivatized.

Table 4 – Comparison of HR-PIB Compositions, Nominal Number Average Molecular Weight of 2400

Solvent wt.%	PDI (@DP 25 psi)	Solvent wt.%	PDI (@DP 65 psi)
0.03	2.68	0.00	2.13
3.51	2.59	0.57	2.11
5.88	2.42	3.43	2.08
7.71	2.17	9.95	1.94
10.08	2.08		

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Catalyst productivity (efficiency) is unexpectedly improved as compared to prior art systems. In Table 5, the process of the invention is compared with prior art reaction systems. Details as to calculation are summarized in Table 6.

Catalyst productivity ranges anywhere from about 650 lbs polymer/lb catalyst complex up to about 2000 lbs polymer/lb catalyst complex with the process of the invention versus from about 150 lbs polymer/lb catalyst complex to about 300 lbs polymer/lb catalyst complex as reported in the prior art. When calculated based on BF_3 only, similar increases in productivity are provided.

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Table 5 - Comparison of Catalyst Productivity

Source	Ex.	TON lbs polymer/ lbs catalyst complex	TON - BF_3 lbs polymer/ lbs BF_3	Mn Daltons
Table 1	16	1003.8	1476.1	1087
U.S. Patent No.				
7038008	1	323.04	888.07	2387
7038008	2	115.84	318.45	956
7217773	comp	171.72	321.21	980
7217773	1	204.6	405.06	930
7485764	1	238.48	407.52	1150
7485764	2	189.11	407.52	1070
7485764	3	157.15	407.52	1030

Table 6 - Calculation of Catalyst Productivity

Source	Ex.	Alcohol	BF ₃	BF ₃	Alcohol	Alcohol	Alcohol	Total Complex	Isobutylene	Conversion	PIB	TON
							wt (lbs)	wt				lbs polymer/ lbs complex
Table 1	16	Methanol					0.129608	0.060992		w/w %	lbs/min	
U.S. Patent No.								0.1906	flow		191	1003.8
7038008	1	2-butanol	mmoles	7.1	mmoles	mmoles	(gms)	(gms)			g/min	
7038008	2	2-butanol	19.8	1.34244	31.68	11.36	2.3481216	1.3233832	450	0.95	427.5	323.04
7217773	comp	Methanol	8.55	0.57969	15.75	5.0463	1.0843	3.6905616	450	0.95	427.5	115.84
7217773	1	Methanol	6.78	0.459684	14.06	0.4504824	0.9102	1.0843	196	0.95	186.2	171.72
7485764	1	Methanol	10	0.678	15	0.4806	1.1586	0.9102	196	0.95	186.2	204.6
7485764	2	Ethanol	10	0.678	17	0.78302	1.46102	1.1586	307	0.9	276.3	238.48
7485764	3	Isopropanol	10	0.678	18	1.08018	1.75818	1.46102	307	0.9	276.3	189.11
								1.75818	307	0.9	276.3	157.15

From the foregoing, it will be appreciated that conversion unexpectedly increases with increased recirculation rates at the same residence time, contrary to the teachings of the prior art. Higher yield is realized without significant additional capital or processing costs. It was also found that polydispersity decreases with substantially the same residence time as circulation rates increase all other things being equal. Also with the inventive process, products produced have unexpectedly lower polydispersities especially at higher molecular weight, and without high levels of solvent also contrary to the teachings of the prior art.

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A particularly useful unexpected result is that alpha content does not decrease with increasing conversion when a high velocity system is used to make the product.

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While the invention has been described in detail, modifications within the spirit and scope of the invention will be readily apparent to those of skill in the art. In view of the foregoing discussion, relevant knowledge in the art and references discussed above in connection with the Background and Detailed Description, the disclosures of which are all incorporated herein by reference, further description is deemed unnecessary. In addition, it should be understood that aspects of the invention and portions of various embodiments may be combined or interchanged either in whole or in part. Furthermore, those of ordinary skill in the art will appreciate that the foregoing description is by way of example only, and is not intended to limit the invention.

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CLAIMS:

1. A method of making a polyisobutylene polymer in a recirculating loop reactor with one or more reaction tubes in contact with a heat transfer medium comprising:

- (a) providing a feed mixture consisting essentially of polymerizable monomer and catalyst to a residual reactor stream at a feed rate to form a reaction mixture, the reaction mixture containing less than 5% by weight diluent components;
- (b) recirculating the reaction mixture in the one or more reaction tubes of the loop reactor at a recirculation rate greater than the feed rate utilizing a recirculating pump operating at a pressure differential, ΔP , corresponding to a recirculating flow;
- (c) polymerizing the reaction mixture in the one or more tubes of the loop reactor to convert the feed mixture to polyisobutylene polymer while cooling the one or more tubes of the loop reactor with the heat transfer medium; and
- (e) withdrawing polyisobutylene polymer from the loop reactor,

with the further proviso that either (i) ΔP and polymerization reaction are controlled to provide a linear velocity of the reaction mixture of at least 3 m/s (10 ft/sec) in the one or more reaction tubes of the loop reactor or (ii) the recirculating pump operating at a pressure differential, ΔP , of from 241 kPa to 552 kPa (35 psi to 80 psi) and controlling the pressure ΔP and polymerization reaction of steps (b) and (c) to provide a recirculation ratio of the recirculation rate to the feed rate of at least 30:1.

2. The method according to Claim 1, wherein the feed mixture and the reaction mixture contain 1.5% by weight or less diluent components.
3. The method according to Claim 1, wherein the feed mixture and the reaction mixture contain 1% by weight or less diluent components.
4. The method according to Claim 1, wherein the delta P and polymerization reaction are controlled to provide a linear velocity of the reaction mixture of at least 3 m/s (10 ft/sec) in the one or more reaction tubes of the loop reactor.
5. The method according to Claim 4, wherein the delta P and polymerization reaction are controlled to provide a linear velocity of the reaction mixture of at least 3.7 m/s (12 ft/sec) in the one or more reaction tubes of the loop reactor.
6. The method according to Claim 1, wherein the polyisobutylene withdrawn from the loop reactor is a highly reactive polyisobutylene with a number average molecular weight of from 500 to 4000 Daltons.
7. The method according to Claim 1, wherein the polymer withdrawn from the loop reactor is a mid-range vinylidene polyisobutylene polymer with a number average molecular weight of from 500 Daltons to 4000 Daltons.
8. The method according to Claim 7, wherein the loop reactor is operated with a catalyst turnover number of from 1600 kg polymer/kg catalyst (lbs. polymer/lbs. catalyst) to 3000 kg polymer/kg catalyst (lbs. polymer/lbs. catalyst).
9. The method according to Claim 1 comprising:

recirculating the reaction mixture in the one or more reaction tubes of the loop reactor at a recirculation rate utilizing a recirculating pump operating at a pressure differential, ΔP , of from 241 kPa to 552 kPa (35 psi to 80 psi);

controlling the pressure Δ and polymerization reaction of steps (b) and (c) to provide a recirculation ratio of the recirculation rate to the feed rate of at least 30:1.

10. The method according to Claim 9, wherein the conversion of isobutylene monomer to polymer is from 50% to 80%.
11. The method according to Claim 9, wherein the ΔP of the recirculating pump is at least 345 kPa (50 psi).
12. The method according to Claim 11, wherein the ΔP of the recirculating pump is at least 414 kPa (60 psi).
13. The method according to Claim 9, operated at a recirculation ratio of from 30:1 to 50:1.
14. The method according to Claim 13, operated at a recirculation ratio of at least 35:1.
15. The method according to any of Claims 1 through 14, operated continuously at a residence time of from 3 to 6 minutes.