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(54) Title: PROCESS FOR PRODUCTION OF HIGH-ISOPRENE BUTYL RUBBER

(57) Abrégé/Abstract:

The present invention relates to a continuos process for producing polymers at conversions ranging from 50 % to 95 % having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and a suitable, proton source (e.g. water) or cationogen and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds and organic nitro compounds.

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**ABSTRACT**

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The present invention relates to a continuos process for producing polymers at conversions ranging from 50 % to 95 % having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from 10 at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and a suitable proton source (e.g. water) or cationogen and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds and organic nitro compounds.

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## PROCESS FOR PRODUCTION OF HIGH-ISOPRENE BUTYL RUBBER

### FIELD OF THE INVENTION

The present invention relates to a continuos process for producing polymers at conversions ranging from 50 % to 95 % with a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and a suitable proton source (e.g. water) or cationogen and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds and organic nitro compounds.

Preferably the polymers have a multiolefin content of greater than 4.1 mol%, and a gel content of less than 10 wt.% and have been produced at conversions ranging from 70 % to 95%. Preferably, the polymers have a Mooney viscosity in the range of from 25-70 MU, more preferably 30-60 MU, even more preferably 30-55 MU.

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### BACKGROUND OF THE INVENTION

Butyl rubber is understood to be a copolymer of an isoolefin and one or more, preferably conjugated, multiolefins as comonomers. Commercial butyl comprise a major portion of isoolefin and a minor amount, not more than 2.5 mol %, of a conjugated multiolefin. The preferred isoolefin is isobutylene. However, this invention 20 also covers polymers optionally comprising additional copolymerizable co-monomers.

Butyl rubber or butyl polymer is generally prepared in a slurry process using methyl chloride as a vehicle and a Friedel-Crafts catalyst as part of the polymerization initiator. The methyl chloride offers the advantage that  $\text{AlCl}_3$ , a relatively inexpensive 25 Friedel-Crafts catalyst, is soluble in it, as are the isobutylene and isoprene comonomers. Additionally, the butyl rubber polymer is insoluble in the methyl chloride and precipitates out of solution as fine particles. The polymerization is generally carried out at temperatures of about -90°C to -100°C. See U.S. Patent No. 2,356,128 and *Ullmanns Encyclopedia of Industrial Chemistry*, volume A 23, 1993, pages 288-295. 30 The low polymerization temperatures are required in order to achieve molecular weights which are sufficiently high for rubber applications.

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Raising the reaction temperature or increasing the quantity of isoprene in the monomer feed results in poorer product properties, in particular, in lower molecular weights. However, a higher degree of unsaturation would be desirable for more efficient crosslinking with other, highly unsaturated diene rubbers (BR, NR or SBR).

5 The molecular weight depressing effect of diene comonomers may, in principle, be offset by still lower reaction temperatures. However, in this case the secondary reactions, which result in gelation occur to a greater extent and these processes are more costly. Gelation at reaction temperatures of around -120°C and possible options for the reduction thereof have been described (*c.f.* W.A. Thaler, D.J. Buckley Sr., Meeting of  
10 the Rubber Division, ACS, Cleveland, Ohio, May 6-9, 1975, published in *Rubber Chemistry & Technology* 49, 960-966 (1976)). The auxiliary solvents such as CS<sub>2</sub> required for this purpose are not only difficult to handle, but must also be used at relatively high concentrations. A further disadvantage associated with the use of CS<sub>2</sub> lies in the fact that polymerization reactions of this type are homogeneous in nature.  
15 Consequently, there are significant increases in solution viscosity as the polymerization reaction proceeds. This in turn necessitates carrying out these polymerizations to lower conversions (i.e. lower amounts of polymer per unit volume of solvent and therefore a cost disadvantage) as high solution viscosities give rise to heat transfer problems.

It is furthermore known to perform gel-free copolymerization of isobutene with  
20 various comonomers to yield products of a sufficiently high molecular weight for rubber applications at temperatures of around -40°C using pretreated vanadium tetrachloride (EP-A1-818 476), a combination of nitro compounds and vanadium (EP-A-1 122 267) or zirconium compounds (WO-02/18460-A1) and others.

This invention operates in the absence of vanadium-, zirconium- and/or hafnium  
25 compounds.

Halogenated butyls are well known in the art, and possess outstanding properties such as oil and ozone resistance and improved impermeability to air. Commercial halobutyl rubber is a halogenated copolymer of isobutylene and up to about 2.5 mol % of isoprene.

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## SUMMARY OF THE INVENTION

In one aspect, the present invention provides a continuos process for producing polymers having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt. % comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol % of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and a proton source and/or cationogen capable of initiating the polymerization process and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds.

In still another aspect, the present invention provides a continuos slurry process for producing polymers having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from isobutene monomer, more than 4.1 mol% of repeating units derived from isoprene monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and a proton source and/or cationogen capable of initiating the polymerization process and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds and organic nitro compounds.

## DETAILED DESCRIPTION OF THE INVENTION

The Mooney viscosity of the polymer is determined using ASTM test D1646 using a large rotor at 125 °C, a preheat phase of 1 min, and an analysis phase of 8 min (ML1+8 @ 125 °C)

The invention is not limited to a special isoolefin. However, isoolefins within the range of from 4 to 16 carbon atoms, in particular 4-7 carbon atoms, such as isobutene, 2-methyl-1-butene, 3-methyl-1-butene, 2-methyl-2-butene, 4-methyl-1-pentene and mixtures thereof are preferred. Most preferred is isobutene.

The invention is not limited to a special multiolefin. Every multiolefin copolymerizable with the isoolefin known by the skilled in the art can be used. However, multiolefins with in the range of from 4-14 carbon atoms, such as isoprene, butadiene, 2-methylbutadiene, 2,4-dimethylbutadiene, piperyline, 3-methyl-1,3-pentadiene, 2,4-hexadiene, 2-neopentylbutadiene, 2-methyl-1,5-hexadiene, 2,5-dimethyl-2,4-hexadiene, 2-methyl-1,4-pentadiene, 2-methyl-1,6-heptadiene,

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cyclopenta-diene, methylcyclopentadiene, cyclohexadiene, 1-vinyl-cyclohexadiene and mixtures thereof, in particular conjugated dienes, are preferably used. Isoprene is particularly preferably used.

5 In the present invention,  $\beta$ -pinene can also be used as a co-monomer for the isoolefin.

As optional monomers every monomer copolymerizable with the isoolefins and/or dienes known by the skilled in the art can be used.  $\alpha$ -methyl styrene, *p*-methyl styrene, chlorostyrene, cyclopentadiene and methylcyclopentadiene are preferably used. Indene and other styrene derivatives may also be used in this invention

10 The multiolefin content is at least greater than 4.1 mol%, more preferably greater than 5.0 mol%, even more preferably greater than 6.0 mol%, yet even more preferably greater than 7.0 mol%.

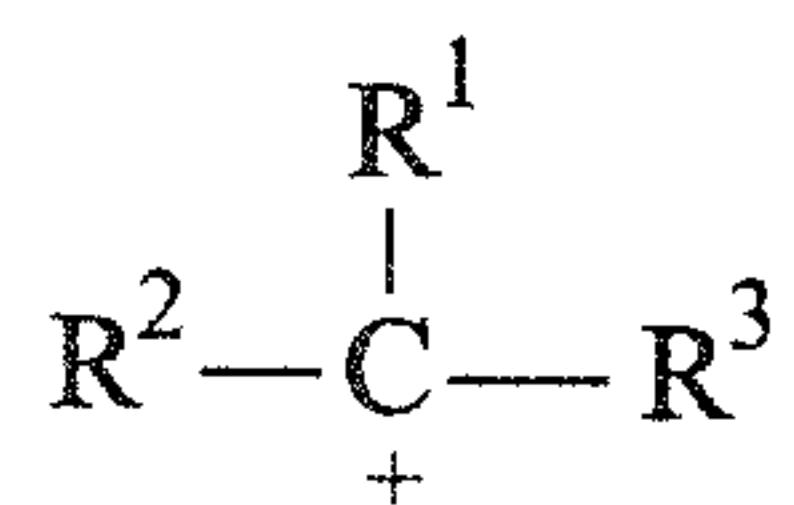
15 Preferably, the monomer mixture comprises in the range of from 80% to 95% by weight of at least one isoolefin monomer and in the range of from 4.0% to 20% by weight of at least one multiolefin monomer including  $\beta$ -pinene and in the range of from 0.01% to 1% by weight of at least one multiolefin cross-linking agent. More preferably, the monomer mixture comprises in the range of from 83% to 94% by weight of at least one isoolefin monomer and in the range of from 5.0% to 17% by weight of a multiolefin monomer or  $\beta$ -pinene and in the range of from 0.01% to 1% by weight of at 20 least one multiolefin cross-linking agent. Most preferably, the monomer mixture comprises in the range of from 85% to 93% by weight of at least one isoolefin monomer and in the range of from 6.0% to 15% by weight of at least one multiolefin monomer, including  $\beta$ -pinene and in the range of from 0.01% to 1% by weight of at least one multiolefin cross-linking agent.

25 The weight average molecular weight,  $M_w$ , is preferably greater than 240 kg/mol, more preferably greater than 300 kg/mol, even more preferably greater than 500 kg/mol, yet even more preferably greater than 600 kg/mol.

30 In connection with this invention the term "gel" is understood to denote a fraction of the polymer insoluble for 60 min in cyclohexane boiling under reflux. The gel content is preferably less than 10 wt.%, more preferably less than 5 wt%, even more preferably less than 3 wt%, yet even more preferably less than 1 wt%.

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The polymerization is performed in the presence of  $\text{AlCl}_3$  and a proton source and/or cationogen capable of initiating the polymerization process. A proton source within the limits of this invention is any compound that will produce a proton when added to  $\text{AlCl}_3$  or a composition containing  $\text{AlCl}_3$ . Protons may be generated from the reaction of  $\text{AlCl}_3$  with proton sources such as water, alcohol or phenol to produce the proton and the corresponding by-product. Such reaction may be preferred in the event that the reaction of the proton source is faster with the protonated additive as compared with its reaction with the monomers. Other proton generating reactants include thiols, carboxylic acids, and the like. In another embodiment, when low molecular weight polymer product is desired an aliphatic or aromatic alcohol is preferred. The most preferred proton source is water. The preferred ratio of  $\text{AlCl}_3$  to water is between 5:1 to 100:1 by weight. It might be advantageous to further introduce from  $\text{AlCl}_3$  deriveable catalyst systems, diethylaluminium chloride, ethylaluminium chloride, titanium tetrachloride, stannous tetrachloride, boron trifluoride, boron trichloride, or methylalumoxane. In addition or instead of a proton source a cationogen capable of initiating the polymerisation process can be used. A cationogen within the limits of this invention is any compound that generates a carbo-cation under the conditions present. A preferred group of cationogens consists of carbocationic compounds having the formula:



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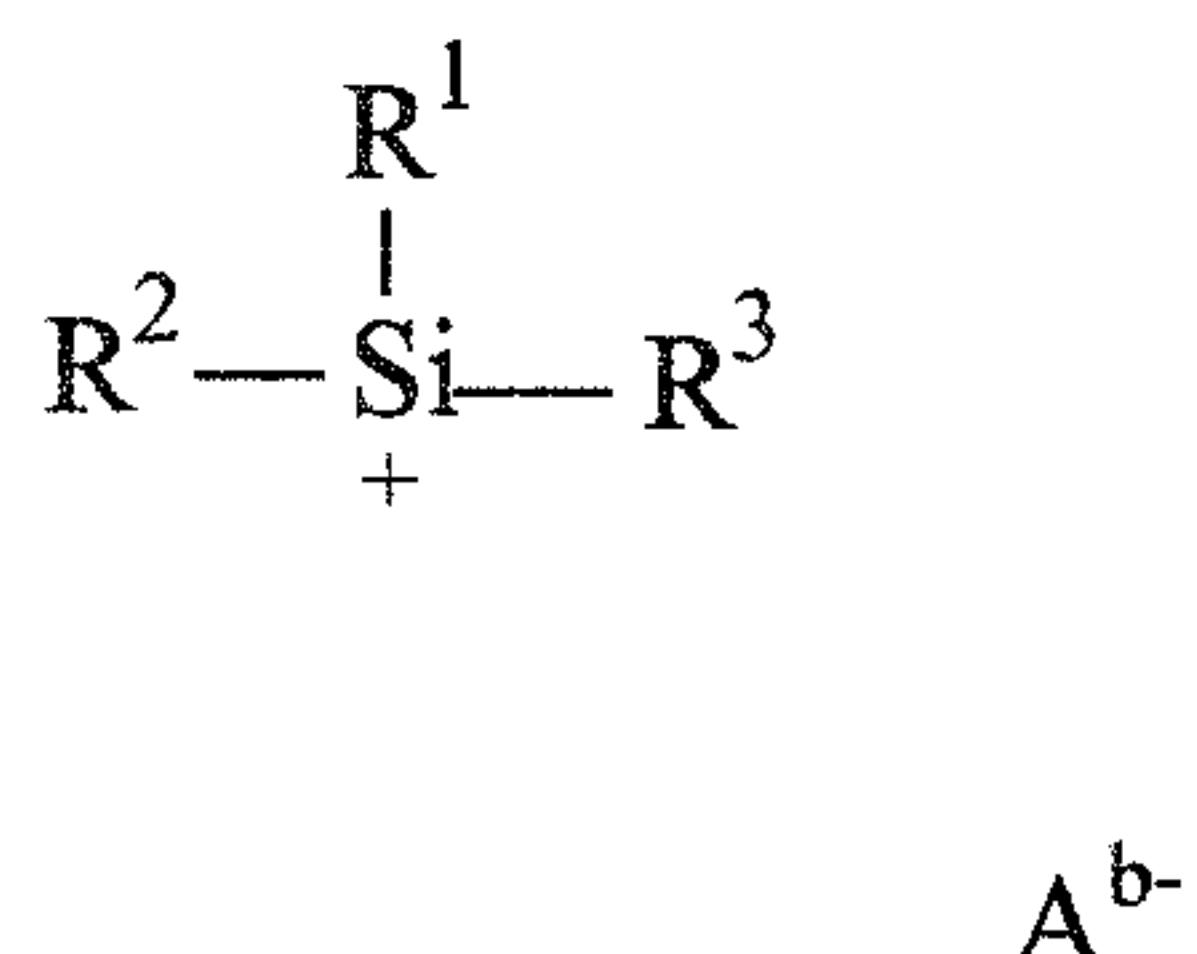
 $\text{A}^{\text{b-}}$ 

wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ , are independently hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  may be hydrogen. Preferably,  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ , are independently a  $\text{C}_1$  to  $\text{C}_{20}$  aromatic or aliphatic group. Non-limiting examples of suitable aromatic groups may be selected

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from the group consisting of phenyl, toyl, xylyl and biphenyl. Non-limiting examples of suitable aliphatic groups are selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl.

5 Another preferred group of cationogens consists of substituted silylum cationic compounds having the formula:



wherein  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$ , are independently hydrogen, or a linear, branched or cyclic aromatic or aliphatic group, with the proviso that only one of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  may be hydrogen. Preferably, none of  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are H. Preferably,  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are, independently, a  $\text{C}_1$  to  $\text{C}_{20}$  aromatic or aliphatic group. More preferably,  $\text{R}^1$ ,  $\text{R}^2$  and  $\text{R}^3$  are independently a  $\text{C}_1$  to  $\text{C}_8$  alkyl group. Examples of useful aromatic groups may be selected from the group consisting of phenyl, toyl, xylyl and biphenyl. Non-limiting examples of useful aliphatic groups may be selected from the group consisting of methyl, ethyl, propyl, butyl, pentyl, hexyl, octyl, nonyl, decyl, dodecyl, 3-methylpentyl and 3,5,5-trimethylhexyl. A particularly preferred group of reactive substituted silylum cations may be selected from the group consisting of trimethylsilylum, triethylsilylum and benzyldimethylsilylum. Such cations may be prepared, for example, by the exchange of the hydride group of the  $\text{R}^1\text{R}^2\text{R}^3\text{Si-H}$  with a non-coordinating anion (NCA), such as  $\text{Ph}_3\text{C}^+\text{B}(\text{pfp})_4^-$  yielding compositions such as  $\text{R}^1\text{R}^2\text{R}^3\text{SiB}(\text{pfp})_4$  which in the appropriate solvent obtain the cation.

In the limits of this invention,  $\text{A}^{\text{b}-}$  denotes an anion. Specifically, preferred anions are those comprised of a single coordination complex possessing a charge

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bearing metal or metalloid core which is negatively charged to the extent necessary to balance the charge on the active catalyst species which may be formed when the two components are combined. More preferably  $A^{b-}$  corresponds to a compound with the general formula  $[MQ_4]^-$  wherein

5 M is a boron, aluminum, gallium or indium in the +3 formal oxidation state; and  
Q is independently selected from hydride, dialkylamido, halide, hydrocarbyl,  
hydrocarbyloxide, halo-substituted hydrocarbyl, halo-substituted hydrocarbyloxide, and  
halo-substituted silylhydrocarbyl radicals.

There are no organic nitro compounds or transition metals used in this process.

10 The reaction mixture used to produce the present butyl polymer further  
comprises a multiolefin cross-linking agent. The term cross-linking agent is known to  
those skilled in the art and is understood to denote a compound that causes chemical  
cross-linking between the polymer chains in opposition to a monomer that will add to  
the chain. Some easy preliminary tests will reveal if a compound will act as a monomer  
15 or a cross-linking agent. The choice of the cross-linking agent is not particularly  
restricted. Preferably, the cross-linking comprises a multiolefinic hydrocarbon  
compound. Examples of these are norbornadiene, 2-isopropenylnorbornene, 2-vinyl-  
norbornene, 1,3,5-hexatriene, 2-phenyl-1,3-butadiene, divinylbenzene,  
20 diisopropenylbenzene, divinyltoluene, divinylxylene and  $C_1$  to  $C_{20}$  alkyl-substituted  
derivatives thereof. More preferably, the multiolefin crosslinking agent is divinyl-  
benzene, diisopropenylbenzene, divinyltoluene, divinyl-xylene and  $C_1$  to  $C_{20}$  alkyl  
substituted derivatives thereof, and or mixtures of the compounds given. Most  
preferably the multiolefin crosslinking agent comprises divinylbenzene and  
diisopropenylbenzene.

25 The polymerization is performed in a continuous process in slurry (suspension),  
in a suitable diluent, such as chloroalkanes as described in US 5,417,930.

The monomers are generally polymerized cationically, preferably at  
temperatures in the range from -120°C to +20°C, preferably in the range from -100°C  
to -20°C, and pressures in the range from 0.1 to 4 bar.

30 The use of a continuous reactor as opposed to a batch reactor seems to have a  
positive effect on the process. Preferably, the process is conducted in at least one

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continuous reactor having a volume of between 0.1 m<sup>3</sup> and 100 m<sup>3</sup>, more preferable between 1 m<sup>3</sup> and 10 m<sup>3</sup>.

Inert solvents or diluents known to the person skilled in the art for butyl polymerization may be considered as the solvents or diluents (reaction medium). These comprise alkanes, chloroalkanes, cycloalkanes or aromatics, which are frequently also mono- or polysubstituted with halogens. Hexane/chloroalkane mixtures, methyl chloride, dichloromethane or the mixtures thereof may be mentioned in particular. Chloroalkanes are preferably used in the process according to the present invention.

Polymerization must be performed continuously. The process is preferably performed with the following three feed streams:

- I) solvent/diluent + isoolefin (preferably isobutene) + multiolefin (preferably diene, isoprene)
- II) initiator system
- III) multiolefin cross-linking agent

It should be noted that the multiolefin crosslinking agent can also be added in the same feed stream as the isoolefin and multiolefin.

Using the process according to the present invention, it is possible to produce novel transition metal-free polymers having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of AlCl<sub>3</sub> and a proton source and/or cationogen capable of initiating the polymerization process and at least one multiolefin cross-linking agent having elevated double bond contents and simultaneously low gel contents. The double bond content may be determined by proton magnetic resonance spectroscopy.

These polymers may be the starting material for a halogenation process in order to produce halo-butyl polymers. Especially preferred are partially or fully chlorinated or brominated polymers having a Mooney viscosity of at least 30 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers wherein the polymer does not contain any transition metal catalyst residues or organic nitro

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compounds residues. These form a further object of the invention. Bromination or chlorination can be performed according to the procedures described in Rubber Technology, 3<sup>rd</sup> Ed., Edited by Maurice Morton, Kluwer Academic Publishers, pp. 297 – 300 and references cited within this reference.

5 The copolymers presented in this invention are ideally suitable for the production of moldings of all kinds, in particular tyre components and industrial rubber articles, such as bungs, damping elements, profiles, films, coatings. The polymers are used to this end in pure form or as a mixture with other rubbers, such as NR, BR, HNBR, NBR, SBR, EPDM or fluororubbers. The preparation of these compounds is  
10 known to those skilled in the art. In most cases carbon black is added as filler and a sulfur based curing system is used. For the compounding and vulcanization it is referred to Encyclopedia of Polymer Science and Engineering, Vol. 4, S. 66 et seq. (Compounding) and Vol. 17, S. 666 et seq. (Vulcanization).

15 The vulcanization of the compounds is usually effected at temperatures in the range of 100 to 200°C, preferred 130 to 180°C (optionally under pressure in the range of 10 to 200 bar).

The following Examples are provided to illustrate the present invention:

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**Examples*****Equipment***

5 Polymer unsaturation was determined through  $^1\text{H}$  NMR spectroscopy with the use of a Bruker  $^1\text{H}$  NMR spectra were obtained on a Bruker 500 MHz NMR Spectrometer. NMR samples used to determine isoprene content were prepared in  $\text{CDCl}_3$ . NMR samples used to determine DVB content were prepared in  $\text{THF-d}_8$ . Microstructure information was calculated with the use of previously established integration methods. Peak shifts were referenced to a TMS internal standard.

10 GPC analysis was performed with the use of a Waters Alliance 2690 Separations Module and Viscotek Model 300 Triple Detector Array. GPC samples were prepared by dissolution in THF.

15 Polymer gel content was determined through conventional gravimetric analysis of the dry, hydrocarbon-insoluble fraction (insoluble in boiling cyclohexane, under agitation for a period of 60 minutes).

***Chemicals***

**Isobutene** was purified to a level which, to those skilled in the art, is amenable to the production of butyl rubber.

20 **Isoprene** was obtained from Exxon Chemical Co and used as received. Isoprene dimer levels were found to be ca. 200 ppm.

**Methyl chloride** was obtained from Dow Chemical Co. and was dried with the use of deactivated alumina gel prior to use.

25 **DVB** (64 % pure divinyl-benzene, Dow Chemical Co.) was used. The composition and purity of this DVB was verified by GC analysis. According to the analysis, this material was found to contain 45 wt % *m*-divinylbenzene (*m*-DVB), 19.5 wt % *p*-divinyl-benzene (*p*-DVB), 24 wt % *m*-ethylvinylbenzene and 11.5 wt % *p*-ethylvinylbenzene

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**Example 1**

The following example illustrates our ability to produce, via a continuous process, a novel grade of IIR possessing an isoprene content of up to 5.0 mol % and Mooney viscosity (ML 1+8 @ 125 °C) between 35 and 40 MU.

5        The monomer feed composition was comprised of 2.55 wt. % of isoprene (IP or IC5) and 27.5 wt. % of isobutene (IP or IC4). This mixed feed was introduced into the continuous polymerization reactor at a rate of 5900 kg/hour. In additon, DVB was introduced into the reactor at a rate of 5.4 to 6 kg/hour. Polymerization was initiated via the introduction of an AlCl<sub>3</sub>/MeCl solution (0.23 wt. % of AlCl<sub>3</sub> in MeCl) at a rate 10 of 204 to 227 kg/hour. The internal temperature of the continuous reaction was maitned between -95 and -100 °C through the use of an evaporative cooling process. Following suffecient residence within the reactor, the newly formed polymer crumb was separated from the MeCl diluent with the use of an aqeous flash tank. At this point, ca. 1 wt. % of stearic acid was introduced into the polymer crumb. Prior to 15 drying, 0.1 wt. % of Irganox® 1010 was added to the polymer. Drying of the resulting material was accomplished with the use of a conveyor oven. Table 1 details the characteristics of the final material.

**Example 2**

20        The following example illustrates our ability to produce, via a continuous process, a novel grade of IIR possessing an isoprene content of up to 8.0 mol % and Mooney viscosity (ML 1+8 @ 125 °C) between 35 and 40 MU.

25        The monomer feed composition was comprised of 4.40 wt. % of isoprene (IP or IC5) and 25.7 wt. % of isobutene (IP or IC4). This mixed feed was introduced into the continuous polymerization reactor at a rate of 5900 kg/hour. In additon, DVB was introduced into the reactor at a rate of 5.4 to 6 kg/hour. Polymerization was initiated via the introduction of an AlCl<sub>3</sub>/MeCl solution (0.23 wt. % of AlCl<sub>3</sub> in MeCl) at a rate of 204 to 227 kg/hour. The internal temperature of the continuous reaction was maitned between -95 and -100 °C through the use of an evaporative cooling process. 30        Following suffecient residence within the reactor, the newly formed polymer crumb was separated from the MeCl diluent with the use of an aqeous flash tank. At this point, ca. 1 wt. % of Stearic acid was introduced into the polymer crumb. Prior to

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drying, 0.1 wt. % of Irganox® 1010 was added to the polymer. Drying of the resulting material was accomplished with the use of a conveyor oven. Table 2 details the characteristics of the final material.

5

### Example 3

This comparative example illustrates the production of IIR with a total isoprene level of 7.26 mol % via a batch polymerization process. The catalyst solution was prepared by dissolving anhydrous  $\text{AlCl}_3$  (1.739 g, 13 mmol, Aldrich 99.99 %) in methyl chloride (400 mL) at  $-30^\circ\text{C}$ , this solution was stirred for 30 minutes prior to being cooled to  $-95^\circ\text{C}$ . To a 2 L Morton-style reaction vessel cooled to  $-95^\circ\text{C}$  and equipped with a over-head stirrer and T-type thermocouple was added methyl chloride (900 mL), isobutene (85.8 g condensed at  $-95^\circ\text{C}$ ), isoprene (12.3 g) and DVB (0.565 g). To this mixture was added catalyst solution (50 mL) in a single portion to initiate polymerization. The reaction was allowed to proceed for 10 minutes at which point 10 mL of EtOH/NaOH was added to terminate the reaction followed by 1 phr Irganox 1076. The resultant slurry was allowed to warm to room temperature, during this time the methyl chloride and remaining monomers evaporated and hexanes was added to dissolve the polymer. The polymer was recovered from the hexanes cement by steam coagulation then dried on a 2-roll mill at  $135^\circ\text{C}$ . Table 3 details the characteristics of 15 the final material.

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### Example 4

This comparative example illustrates the production of IIR with a total isoprene level of 7.00 mol % via a batch polymerization process in which no crosslinking agent (e.g. DVB) is present. The catalyst solution was prepared by dissolving anhydrous  $\text{AlCl}_3$  (0.3 g, Aldrich 99.99 %) in methyl chloride (200 mL) at  $-30^\circ\text{C}$ , this solution was stirred for 30 minutes prior to being cooled to  $-95^\circ\text{C}$ . To a 2 L Morton-style reaction vessel cooled to  $-95^\circ\text{C}$  and equipped with a over-head stirrer and T-type thermocouple was added methyl chloride (900 mL), isobutene (11.82 g condensed at  $-95^\circ\text{C}$ ), and 25 isoprene (2.04 g). To this mixture was added catalyst solution (22 mL) in a single portion to initiate polymerization. The reaction was allowed to proceed for 10 minutes 30 at which point 10 mL of EtOH/NaOH was added to terminate the reaction followed by

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1 phr Irganox 1076. The resultant slurry was allowed to warm to room temperature, during this time the methyl chloride and remaining monomers evaporated and hexanes was added to dissolve the polymer. The polymer was recovered from the hexanes cement by steam coagulation then dried on a 2-roll mill at 135 °C. Table 4 details the 5 characteristics of the final material.

From these examples it can be seen that the preparation of IIR with elevated levels of IP (IC5) and acceptable Mooney viscosities (35 – 40 MU) can be successfully prepared in a AlCl<sub>3</sub>/H<sub>2</sub>O initiated continuous polymerization process in the presence of DVB 10 (Examples 1 & 2). Although it is possible to prepare IIR with an isoprene content of 7.26 mol in a batch process (with DVB), it is apparent from the data presented in Example 3, that such a material possesses a significantly lower Mooney viscosity, M<sub>w</sub>, and M<sub>z</sub> and is produced at reduced conversions. Similarly, when such a material is produced in the absence of DVB (Example 4), a further reduction in the Mooney and 15 M<sub>w</sub> is observed.

**Table 1.**

Isoprene Content (mol %)	4.5 – 5.0
DVB Content (mol %)	0.07 – 0.11
Mooney Viscosity (MU, ML1+8 @ 125 °C)	35 – 40
Gel Content (wt. %)	< 5.0
M <sub>w</sub> (kg/mol)	450 - 550
M <sub>n</sub> (kg/mol)	200 - 220
M <sub>z</sub> (kg/mol)	900 - 1400
Conversion (%)	77 – 84

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**Table 2.**

Isoprene Content (mol %)	7.0 – 8.0
DVB Content (mol %)	0.07 – 0.11
Mooney Viscosity (MU, ML1+8 @ 125 °C)	35 – 40
Gel Content (wt. %)	< 5.0
$M_w$ (kg/mol)	700 - 900
$M_n$ (kg/mol)	100 -105
$M_z$ (kg/mol)	3200 - 5500
Conversion (%)	77 - 84

**Table 3.**

Isoprene Content (mol %)	7.26
DVB Content (mol %)	0.18
Mooney Viscosity (MU, ML1+8 @ 125 °C)	28
Gel Content (wt. %)	< 5.0
$M_w$ (kg/mol)	427
$M_n$ (kg/mol)	132
$M_z$ (kg/mol)	1026
Conversion (%)	50

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**Table 4.**

Isoprene Content (mol %)	7.0
DVB Content (mol %)	N/A
Mooney Viscosity (MU, ML1+8 @ 125 °C)	15
Gel Content (wt. %)	< 5
$M_w$ (kg/mol)	358
$M_n$ (kg/mol)	140
$M_z$ (kg/mol)	1202
Conversion (%)	78

**Claims**

1. A continuos process for producing polymers at conversion levels ranging between 50 % and 95 % having a Mooney viscosity of at least 25 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol% of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers in the presence of  $\text{AlCl}_3$  and at least one proton source and/or cationogen capable of initiating the polymerization process and at least one multiolefin cross-linking agent wherein the process is conducted in the absence of transition metal compounds and organic nitro compounds.  
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2. A process according to Claim 1, where the polymer is produced at conversion levels ranging from 60 % to 95 and contains greater than 5 mol % of repeat units derived from a multiolefin and a gel content of less than 10 wt. %.  
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3. A process according to Claim 1, where the polymer is produced at conversion levels ranging from 75 % to 95 and contains greater than 7 mol % of repeat units derived from a multiolefin and a gel content of less than 5 wt. %.  
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4. A process according to Claim 1, wherein said isoolefin monomer is isobutene.  
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5. A process according to Claims 1-4, wherein the process is conducted in at least one continuous reactor having a volume between  $0.1 \text{ m}^3$  and  $100 \text{ m}^3$ .  
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6. A process according to Claims 1-4, wherein the process is conducted in a continuous reactor having a volume between  $1 \text{ m}^3$  and  $10 \text{ m}^3$ .
7. A process according to any of the Claims 1-6, wherein said multiolefin is isoprene.  
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8. A process according to any of the Claims 1-6 wherein said multiolefin crosslinking agent is divinylbenzene.

9. A polymer having a Mooney viscosity of at least 30 Mooney-units and a gel content of less than 15 wt.% comprising repeating units derived from at least one isoolefin monomer, more than 4.1 mol % of repeating units derived from at least one multiolefin monomer and optionally further copolymerizable monomers, wherein the polymer does not contain any transition metal catalyst residues or organic nitro compounds residues.

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10. A polymer according to Claim 9 which has been either partially or completely chlorinated.

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11. A polymer according to Claim 9 which has been either partially or completely brominated.

12. A polymer according to either Claim 10 or 11 which has been maleated.

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13. A polymer according to either Claim 10 or 11 which has been functionalized with nucleophilic species such as NR<sub>3</sub>, -OR, -SR, PR<sub>3</sub>, -OPR<sub>3</sub>, -OSiR<sub>3</sub>, -CR<sub>3</sub>, -O<sub>2</sub>CR where R = H, F, Cl, Br, I, C<sub>x</sub>H<sub>2</sub>CH<sub>3</sub> (x = 0 to 20), phenyl (or any aromatic derivative), or cyclohexyl group.