(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
27 December 2012 (27.12.2012)

WIPO | PCT

(10) International Publication Number
WO 2012/175678 A1

(51) International Patent Classification:
C08F 236/10 (2006.01) *C08L 9/06* (2006.01)
C08F 212/08 (2006.01) *C08L 25/10* (2006.01)

(21) International Application Number:
PCT/EP2012/062095

(22) International Filing Date:
22 June 2012 (22.06.2012)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
11170968.9 22 June 2011 (22.06.2011) EP

(71) Applicant *(for all designated States except US)*: **STYRON EUROPE GMBH** [CH/CH]; Bachtobelstrasse 3, CH-8810 Horgen (CH).

(72) Inventors; and
(75) Inventors/Applicants *(for US only)*: **HAMANN, Evemarie** [DE/DE]; Prager Strasse 31a, 06128 Halle (DE). **VALENTI, Silvia** [IT/DE]; Merseburger Strasse 197, 06122 Halle (DE). **HOLTZ, Gabriele** [DE/DE]; c/o Styron Deutschland GmbH, B 13, 06258 Schkopau (DE).

(74) Agents: **HOFFMANN·EITLE, Peter, Wiedemann** et al.; Arabellastrasse 4, 81925 Munich (DE).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

WO 2012/175678 A1

(54) **Title**: HIGH STYRENE HIGH VINYL STYRENE-BUTADIENE RUBBER WITH NARROW MOLECULAR WEIGHT DISTRIBUTION AND METHODS FOR PREPARATION THEREOF

(57) **Abstract**: A polymer having at least the following characteristics: (a) a block styrene content with more than 4 consecutive styrene units from about 40 to about 70 weight percent based on total styrene content in the polymer; (b) a vinyl content from about 25 to about 80 weight percent based on total amount of polymerized 1,3-diene; (c) a styrene content from about 20 to about 75 weight percent based on total weight of polymer; and (d) a molecular weight distribution (Mw/Mn) of 1.5 or less.

HIGH STYRENE HIGH VINYL STYRENE-BUTADIENE RUBBER WITH NARROW MOLECULAR WEIGHT DISTRIBUTION AND METHODS FOR PREPARATION THEREOF

TECHNICAL FIELD

[0001] The present teachings relate generally to high styrene high vinyl solution-based styrene-butadiene rubber (SSBR)—particularly to high styrene high vinyl SSBR with a narrow molecular weight distribution—and to methods for the preparation thereof.

BACKGROUND

[0002] High styrene and high vinyl SSBR is difficult to produce due to the kinetics of copolymerization. Typically, polar agents known as randomizers are added to the polymerization system in order to achieve random styrene incorporation.

[0003] The use of certain randomizers can result in high vinyl SSBR having a low block styrene content (> 6 successive units of styrene) below 10%. Long block styrene can worsen hysteresis as reported, for example, by S. Futamura and G. Day who observed a worsening by about 18% of the tan delta at 60 °C when increasing block styrene content from 2 to about 7% (*Kautschuk Gummi Kunststoffe*, **1987**, *40*, No. 1, 39-43) in a carbon black-filled compound. By contrast, incorporation of small styrene blocks can result in improved abrasion and tensile strengths, particularly in silica compounds, as reported by I. Hattori et al. (*143rd Meeting of the Rubber Division of the ACS*, Spring **1993**, paper 22).

[0004] Potassium 3,7-dimethyl-3-octylate is described in United States Patent No. 6,521,712 for the preparation of random low vinyl soft blocks in block copolymers. Likewise, United States Patent No. 6,197,889 describes the use of potassium 3,7-dimethyl-3-octylate as randomizer. In both patents, the molecular weight of the resulting polymer is very low (range 3000-200,000 g/mol).

[0005] In United States Patent No. 3,294,768, the use of sodium and potassium alcoholates as randomizer for low vinyl SSBR is reported. In

United States Patent No. 3,787,377, sodium and potassium tert-amylate and mentholate are described in the context of continuous anionic polymerization, at a temperature from 110 to 125 °C. United States Patent No. 5,916,962 describes a conjugated rubber composition, which shows a broad molecular weight distribution of 1.7 or more after coupling with silicon tetrachloride.

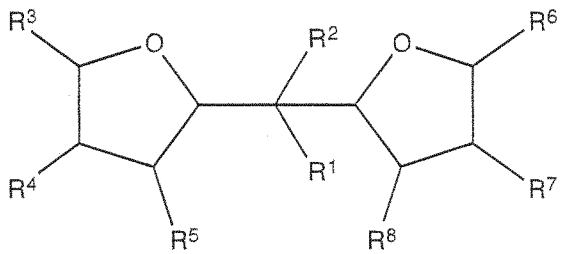
[0006] In certain applications, it would be desirable to achieve a high styrene high vinyl SSBR having a defined incorporation of styrene as blocks of more than 4 consecutive styrene units with a narrow molecular weight distribution.

SUMMARY

[0007] The scope of the present invention is defined solely by the appended claims, and is not affected to any degree by the statements within this summary.

[0008] By way of introduction, a polymer embodying features of the present teachings has at least the following characteristics: (a) a block styrene content containing more than 4 consecutive styrene units from about 40 to about 70 weight percent based on total styrene content in the polymer; (b) a vinyl content from about 25 to about 80 weight percent based on total amount of polymerized 1,3-butadiene; (c) a styrene content from about 20 to about 75 weight percent based on total weight of polymer; and (d) a molecular weight distribution D (Mw/Mn) of 1.5 or less.

[0009] A process for polymerization of a polymer comprising monomeric units derived from a styrene monomer and a 1,3-butadiene monomer that embodies features of the present teachings includes polymerizing the monomeric units in the presence of an initiator, a potassium alcoholate and a polar agent. The polar agent comprises a structure I:



(I);

[0010] wherein R^1 and R^2 are each independently an alkyl group; wherein R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of an alkyl group and hydrogen.

DETAILED DESCRIPTION

[0011] The present inventors have discovered—surprisingly and unexpectedly—a high styrene, high vinyl SSBR with a narrow molecular weight distribution, an incorporation of styrene in blocks of more than 4 consecutive styrene units ranging from about 40 to about 70%, and further features as described below.

[0012] Moreover, the present inventors have further discovered—surprisingly and unexpectedly—that it is possible to prepare the above-described high styrene high vinyl SSBR using an initiator (e.g., butyl lithium) and a randomizer (e.g., ditetrahydrofurylpropane, also known as 2,2-di(2-oxolanyl)propane or DOP) in combination with a potassium alcoholate, in some embodiments, under the following conditions: styrene content ≥ 20 wt%; molar ratio of potassium alcoholate/active initiator ≥ 0.05; and polymerization temperature ≤ 80 °C.

[0013] Throughout this description and in the appended claims, the following definitions are to be understood:

[0014] The term "polymer" refers broadly to a material prepared via the polymerization of monomeric units. As used herein, the term "polymer" subsumes the terms "homopolymer" (polymeric material prepared from a single type of monomer), "copolymer" (polymeric material prepared from two different types of monomers), and "interpolymer" (polymeric material prepared from more than two different types of monomers).

[0015] The phrase "alkyl group" refers to a substituted or unsubstituted, straight, branched or cyclic hydrocarbon chain containing, preferably, from 1 to 20 carbon atoms. Representative examples of unsubstituted alkyl groups for use in accordance with the present teachings include but are not limited to methyl, ethyl, propyl, *iso*-propyl, cyclopropyl, butyl, *iso*-butyl, *tert*-butyl, *sec*-butyl, cyclobutyl, and the like.

[0016] The term "process" used in reference to polymerization reactions includes batch, semi-batch, and/or continuous processes.

[0017] The phrase "batch-" or "semi-batch" used in reference to a polymerization refers to a polymerization in which more than 60% of the solvent is charged in the reactor together with additional polymerization ingredients before start of the polymerization by charge of the initiator. The monomer can be charged at once before the addition of initiator, partially before the addition of initiator, partially after the addition of initiator or at once continuously after addition of the initiator over a certain time period.

[0018] The phrase "continuous polymerization" refers to a polymerization process in which the solvent, monomer(s), and any additional polymerization ingredients are fed in a continuous matter to a reactor in specified volumetric ratios. In some embodiments, two or more polymerization reactors connected in series are used. In some embodiments, reagents are fed to only one reactor.

[0019] The phrase "vinyl content" refers to a mass (or weight) percentage of butadiene incorporated in the 1,2 position in the polymer chain, and is based on the butadiene portion (total amount of polymerized butadiene) in the polymer.

[0020] The phrase "styrene content" refers to a mass (or weight) percentage of styrene in the polymer, and is based on the total weight of the polymer.

[0021] The phrase "block styrene content" refers to a weight fraction of styrene incorporated as consecutive sequences of styrene units based on the total amount of polymerized styrene in the polymer.

[0022] The term "composition" refers to a mixture of materials including a polymer material and, optionally, reaction products and/or decomposition products formed from the polymer material.

[0023] The term "active initiator" (nBL,pm) refers to the molar amount of initiator (e.g., an organolithium) that takes part in a polymerization reaction and that is not deactivated by impurities contained in the reaction medium.

The term "excess initiator" (nBL,exc) refers to the molar amount of initiator that is charged to deactivate the impurities in the system.

[0024] The phrase "total amount of monomer feed" refers to the total amount of styrene and butadiene, in g/min, fed in a continuous polymerization reactor and, typically, in the first continuous polymerization reactor.

[0025] The phrase "total monomer conversion" refers to the final monomer conversion (e.g., the final sum conversion of styrene and butadiene) determined for the last polymerization reactor and/or at the end of the polymerization reaction.

[0026] By way of general introduction, a polymer in accordance with the present teachings has at least the following characteristics: (a) a block styrene content containing more than 4 consecutive styrene units from about 40 to about 70 weight percent based on total styrene content in the polymer; (b) a vinyl content from about 25 to about 80 weight percent based on total amount of polymerized 1,3-butadiene; (c) a styrene content from about 20 to about 75 weight percent based on total weight of polymer; and (d) a molecular weight distribution of 1.5 or less.

[0027] In some embodiments, a polymer in accordance with the present teachings has a block styrene content with more than 6 consecutive styrene units of between about 5 and about 30 weight percent based on total styrene content in the polymer.

[0028] In some embodiments, a polymer in accordance with the present teachings has an overall styrene content of between about 25 and about 65 weight percent, and in some embodiments between about 50 and 60 weight percent.

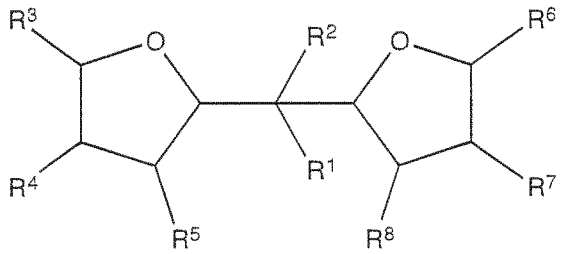
[0029] In some embodiments, the polymer is produced in a batch process, and in some embodiments, it is produced continuously. Presently preferred, however, is a batch process. The polymer in accordance with the present teachings has a molecular weight distribution (Mw/Mn) of 1.5 or less, such as from about 1.05 to about 1.4. In some embodiments, the molecular weight distribution is from about 1.1 to about 1.4. In some embodiments, the molecular weight distribution is from about 1.2 to about 1.35.

[0030] In some embodiments, a polymer in accordance with the present teachings has a number-average molecular weight greater than or equal to about 200,000 g/mole. In some embodiments, the number-average molecular weight is greater than or equal to about 400,000 g/mole. In some embodiments, the number-average molecular weight is greater than or equal to about 550,000 g/mole.

[0031] In some embodiments, a polymer in accordance with the present teachings has a weight-average molecular weight greater than or equal to about 250,000 g/mole. In some embodiments, the weight-average molecular weight is greater than or equal to about 500,000 g/mole. In some embodiments, the weight-average molecular weight is greater than or equal to about 600,000 g/mole.

[0032] All embodiments described above are to be understood as being disclosed in any combination, including combinations of presently preferred embodiments.

[0033] By way of further general introduction, a process for polymerization of a polymer comprising monomeric units derived from a styrene monomer and a 1,3-butadiene monomer in accordance with the present teachings includes polymerizing the monomeric units in the presence of an initiator, a potassium alcoholate and a polar agent, wherein the polar agent comprises a structure I:



(I).

[0034] In some embodiments, R^1 and R^2 are each independently an alkyl group. In some embodiments, R^1 and R^2 are each independently a C_1-C_4 alkyl group. In some embodiments, R^1 and R^2 are each methyl.

[0035] In some embodiments, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of an alkyl group and

hydrogen. In some embodiments, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of hydrogen and a C_1-C_4 alkyl group. In some embodiments, R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of hydrogen and methyl. In some embodiments, R^3, R^4, R^5, R^6, R^7 and R^8 are each hydrogen.

[0036] In some embodiments, a molar ratio of the polar agent to active initiator is greater than about 0.1. In some embodiments, a molar ratio of the polar agent to active initiator is between about 0.2 and about 3.

[0037] In some embodiments, the styrene content of a monomer mixture added in the polymerization is greater than about 40 weight percent based on total weight of added monomers.

[0038] In some embodiments, a polymerization in accordance with the present teachings is run at a temperature of less than about 80 °C. In some embodiments, a polymerization in accordance with the present teachings is run at a temperature of between about 10 °C and about 80 °C.

[0039] Initiators that are presently preferred for use in accordance with the present teachings include those suitable for anionic polymerizations. In some embodiments, an initiator for use in accordance with the present teachings is an organolithium (e.g., alkyl lithium). Representative alkyl lithium agents for use in accordance with the present teachings include but are not limited to n-butyl lithium, sec-butyl lithium, tert-butyl lithium, n-pentyl lithium, and the like, and combinations thereof. In some embodiments, the initiator comprises n-butyl lithium.

[0040] In some embodiments, total monomer conversion is greater than about 96 weight percent based on total amount of monomer feed. In some embodiments, total monomer conversion is greater than about 98 weight percent. In some embodiments, total monomer conversion is greater than about 99 weight percent.

[0041] In some embodiments, a polymer in accordance with the present teachings has a vinyl content from about 25 to about 80 weight percent based on total amount of polymerized 1,3-butadiene. In some embodiments, the vinyl content is from about 40 to about 75 weight percent.

[0042] In some embodiments of a process in accordance with the present teachings, the potassium alcoholate comprises potassium-3,7-dimethyl-3-octylate.

[0043] In some embodiments of a process in accordance with the present teachings, the molar ratio of the polar agent to the potassium alcoholate is from about 30:1 to about 1:5.

[0044] The process in accordance with the present teachings enables the preparation of the polymer as described herein.

[0045] It is presently preferred that polymerizations in accordance with the present teachings take place in solvents, with hydrocarbon solvents being presently preferred. In some embodiments, the polymerization solvent comprises an alkane. In some embodiments, the polymerization solvent comprises cyclohexane. In some embodiments, the polymerization solvent comprises a mixture of cyclohexane with one or more additional alkanes.

[0046] By way of further general introduction, a polymer in accordance with the present teachings is formed by a process of a type described herein.

[0047] In some embodiments, a living polymer in accordance with the present teachings can be chemically modified by chain-end modification and/or coupling reactions. The appropriate chain-end modifiers and/or coupling agents can be chosen according to the target application and filler. Representative coupling agents include but are not limited to tin tetrachloride, silicon tetrachloride, divinylbenzene, alkoxysilanes, and the like, and combinations thereof.

[0048] Representative modifying agents include but are not limited to amines, amides, thioglycols, silicon alkoxides, silane-sulfide modifiers, sulfenyl halides as described in European Patent Document No. EP1016674, benzophenone, isocyanate, hydroxyl mercaptans as described in European Patent Document No. EP0464478, acrylamide compounds as described in European Patent Document No. EP0334042, and the like, and combinations thereof. Additional modifiers include but are not limited to amines, amides, imides, and nitriles modifiers as described in European Patent Document Nos. EP548799, EP510410, EP451604, and EP180141, and in U.S. Patent No.

4,412,041. In some embodiments, silanes including but not limited to epoxy-containing silanes are used for modifying the polymer chain end for use in silica fillers as described, for example, in European Patent Document Nos. EP-A-299074, EP-A-102045, EP0447066, and EP0692493. Additional representative modifiers and/or patent references referring to such are provided in International Patent Document No. WO 2009/134665.

[0049] By way of further general introduction, a composition embodying features of the present teachings includes a polymer of a type described herein. In some embodiments, a composition in accordance with the present teachings further includes additives, such as an oil. In some embodiments, a composition in accordance with the present teachings further includes an oil in an amount from about 5 to about 40 weight percent based on weight of the polymer. In some embodiments, a composition in accordance with the present teachings does not include an oil.

[0050] In some embodiments, a composition in accordance with the present teachings includes a polymer of a type described herein and at least one additive. In some embodiments, the polymer is combined and/or reacted with one or more fillers, a vulcanization agent, and/or optionally one or more additional additives including but not limited to accelerators, coupling agents, unmodified, uncrosslinked elastomeric polymers (i.e., conventional uncrosslinked elastomeric polymers that have not been reacted with a modifier, but that have been prepared and terminated), and the like, and combinations thereof.

[0051] In some embodiments, a composition in accordance with the present teachings includes one or more fillers, which serve as reinforcement agents. Representative examples of suitable fillers include but are not limited to carbon black, silica, carbon-silica dual-phase filler, clay, calcium carbonate, magnesium carbonate, and the like, and combinations thereof. In some embodiments, a combination of carbon black and silica, carbon-silica dual-phase-fillers or a combination of carbon-silica dual-phase-filler and carbon black and/or silica are used.

[0052] In some embodiments, carbon black is manufactured by a furnace method, and has a nitrogen adsorption specific surface area from about 50 to about 200 m^2/g, and a DBP oil absorption from about 80 to about 200 ml/100 grams (e.g., FEF, HAF, ISAF or SAF class carbon black). In some embodiments, a "high agglomeration type" carbon black is used. In some embodiments, carbon black or silica is added in an amount from about 2 to about 100 parts by weight for 100 parts by weight of total polymer. In some embodiments, carbon black or silica is added in an amount from about 5 to about 100 parts by weight. In some embodiments, carbon black or silica is added in an amount from about 10 to about 100 parts by weight. In some embodiments, carbon black or silica is added in an amount from about 10 to 95 parts by weight.

[0053] Finally, by way of further general introduction, an article embodying features of the present teachings includes at least one component formed from such a composition. In some embodiments, the article is a tire. In some embodiments, the article is a shoe component.

[0054] The following examples and representative procedures illustrate features in accordance with the present teachings, and are provided solely by way of illustration. They are not intended to limit the scope of the appended claims or their equivalents.

EXAMPLES

[0055] Monomer conversion was determined by measuring the solids concentration of the polymer solution at the end of the polymerization. The maximum solid content is obtained at 100 wt% conversion of the charged butadiene (mBd) and styrene (mSt) for the final polymer by TSC max = (mBd+ mSt)/(mBd + mSt + mpolar agent + mBL+ mcyclohexane)*100%. A sample of polymer solution ranging from about 1 g to about 10 g, depending on the expected monomer conversion, was drawn from the reactor directly into a 200-mL Erlenmeyer flask filled with ethanol (50 mL). The weight of the filled Erlenmeyer flask was determined before sampling ("A") and after sampling ("B"). The precipitated polymer was removed from the ethanol by filtration on

a weighted paper filter (Micro-glass fiber paper, ϕ 90 mm, MUNKTELL, weight "C"), dried at 140 °C, using a moisture analyzer HR73 (Mettler-Toledo) until a constant mass was achieved. The criterion 5 was used. Finally, a second drying period was performed using switch-off criteria 4 to obtain the final mass "D" of the dry sample on the paper filter. The polymer content in the sample was calculated as TSC = (D-C)/(B-A)*100%. The final monomer conversion was calculated as TSC/TSC max*100%.

[0056] Molecular weight and molecular weight distribution of the polymer were each measured using Size Exclusion Chromatography (SEC) based on polystyrene standards. Each polymer sample (9-11 mg) was dissolved in tetrahydrofuran (10 mL) to form a solution. The solution was filtered using a 0.45-µm filter. A 100-µL sample was fed into a GPC column (Hewlett Packard system 1100 with 3 PLgel 10µm MIXED-B columns at 40°C). Refraction Index-detection was used as the detector for analyzing the molecular weight. The molecular weight was calculated as polystyrene based on the calibration with EasiCal PS1 (Easy A and B) Polystyrene standards from Polymer Laboratories. The number-average molecular weight (Mn) figures and the weight-average molecular weight (Mw) figures are given based on the polystyrene standards. The molecular weight distribution is expressed as the dispersity D = Mw/Mn.

[0057] Vinyl and total styrene content were measured using ^{1}H-NMR, following ISO 21561-2005, using a NMR spectrometer BRUKER Avance 400MHz), and a 5-mm dual probe. $CDCl_3$/TMS was used as solvent in a weight ratio of 0.05% : 99.95%. The content of block styrene having more than 6 consecutive styrene units was determined according to the method reported by Y. Tanaka et al. in *Rubber Chemistry and Technology*, **1981**, *54*, No. 4, 685-691 using the relative intensity of ortho Ph-proton signals resonating higher than 6.7 ppm. The content of block styrene having 4 and more consecutive styrene units was determined according to the method described in German Patent Document No. DE69712962 using the relative intensity of the ortho Ph-proton signals resonating in the range between 6.94

and 6 ppm. The content of block styrene having 4 to 6 consecutive units was calculated from the difference between both of the above-described block styrene contents.

[0058] **COMPARATIVE EXAMPLE 1** (Use of K-3,7-dimethyl-3-octylate (KDMO or K in the following) (50% in hexanes))

[0059] 5376.55 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 326.17 g of 1,3-Butadiene, 403.73g of styrene, and 0.083 mmol of K-3,7-dimethyl-3-octylate (50% in heptane) were fed into the reactor (K/active butyl lithium mol/mol=0.076). The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint, the polymerization was started by addition of the total amount of 1.466 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 19 seconds. Then the polymerization started. The temperature in the reactor raised to 65C within 30 minutes. The reaction was finished after 200 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant.

[0060] A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.57% was measured.

[0061] The resulting polymer was analyzed by GPC: Mn= 533636, Mw= 674699, D=1.264. The microstructure and styrene block content was measured by 1H-NMR. The following results were obtained: styrene=55.2%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=12.3%, block styrene having more than 4 styrene units=82%, and block styrene having more than 6 styrene units=39%.

[0062] **COMPARATIVE EXAMPLE 2** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes))

[0063] 5309.09 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 325.38 g of 1,3-Butadiene, 398.27 g of styrene, and 0.5011 mmol of K-3,7-dimethyl-3-octylate (50% in heptane) were fed into the reactor (K/active butyl lithium mol/mol= 0.38).

[0064] The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.236 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 50 seconds. Then the polymerization started. The temperature in the reactor raised to 65C within 30 minutes. The reaction was finished after 144 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant.

[0065] A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.18% was measured.

[0066] The resulting polymer was analyzed by GPC: Mn=510436, Mw=830705, D=1.627. The microstructure and styrene block content was measured by 1H-NMR. The following results were obtained: styrene=50.3%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=24.3%, block styrene having more than 4 styrene units=64%, and block styrene having more than 6 styrene units=20%.

[0067] **EXAMPLE 1** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0068] 5302.55 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 324.98 g of 1,3-Butadiene, 400.62 g of styrene, 0.5051 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 0.4807 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.359, DOP/active butyllithium 0.341). The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.4086 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 33 seconds. Then the polymerization started. The temperature in the reactor raised to 65 °C within 30 minutes. The reaction was finished after 200 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by means of a sampling tube with a stopcock and a needle

for determination of the solid content. A conversion of 99.11% was measured. The resulting polymer was analyzed by GPC: Mn=502096, Mw=742517, D=1.479. The microstructure and styrene block content was measured by ^{1}H-NMR. The following results were obtained: styrene=55.5%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=40%, block styrene having more than 4 styrene units=70%, and block styrene having more than 6 styrene units=24%.

[0069] **EXAMPLE 2** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0070] 5309.09 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 325.38 g of 1,3-Butadiene, 398.27 g of styrene, 0.1265 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 0.4807 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.1, DOP/ active butyl lithium mol/mol=0.398). The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.2366 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 50 seconds. Then the polymerization started. The temperature in the reactor raised to 65 °C within 30 minutes. The reaction was finished after 120 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.18% was measured. The resulting polymer was analyzed by GPC: Mn=606718, Mw=810367, D=1.336. The microstructure and styrene block content was measured by ^{1}H-NMR. The following results were obtained: styrene=54.4%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=37.6%, block styrene having more than 4 styrene units=70%, and block styrene having more than 6 styrene units=24%.

[0071] **EXAMPLE 3** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP

[0072] 5241.71 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 321.48 g of 1,3-Butadiene, 398.25 g of styrene, 0.1198 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 1.1846 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0087, DOP/active butyl lithium mol/mol=0.894). The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.3816 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 50 seconds. Then the polymerization started. The temperature in the reactor raised to 65 °C within 30 minutes. The reaction was finished after 120 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.58% was measured. The resulting polymer was analyzed by GPC: Mn=557928, Mw=722762, D=1.246. The microstructure and styrene block content was measured by ^{1}H-NMR. The following results were obtained: styrene=54.5%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=52%, block styrene having more than 4 styrene units=66%, and block styrene having more than 6 styrene units=20%.

[0073] **EXAMPLE 4** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0074] 5344.73 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 327.57 g of 1,3-Butadiene, 401.18 g of styrene, 0.1222 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 3.531 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.102, DOP/active butyl lithium mo/mol=2.948). The mixture was heated up to 50 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.1978 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 1 minute 46 seconds. Then the polymerization started. The temperature in the reactor

raised to 65 °C within 30 minutes. The reaction was finished after 200 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.13% was measured. The resulting polymer was analyzed by GPC: Mn=659095, Mw=859095, D=1.274. The microstructure and styrene block content was measured by ^{1}H-NMR. The following results were obtained: styrene=55.1%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=63.9%, block styrene having more than 4 styrene units=66%, and block styrene having more than 6 styrene units=19%.

[0075] **EXAMPLE 5** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0076] 5417 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 302.28 g of 1,3-Butadiene, 371 g of styrene, 0.112 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 1.14 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.105, DOP/active butyl lithium mo/mol=1.067). The mixture was heated up to 70 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.07 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within 30 seconds. Then the polymerization started. The temperature in the reactor was kept constant at 70 °C. The reaction was finished after 120 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 98.88% was measured. The resulting polymer was analyzed by GPC: Mn=673082, Mw=880826, D=1.308. The microstructure and styrene block content were measured by ^{1}H-NMR. The following results were obtained: styrene=55.6%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=42.6%, block styrene having more than 4 styrene units=53%, and block styrene having more than 6 styrene units=10%.

[0077] **EXAMPLE 6** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0078] 5387 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 10-liter, stainless steel reactor. 400.52 g of 1,3-Butadiene, 268 g of styrene, 0.111 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 1.117 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.089, DOP/active butyl lithium mo/mol=0.889). The mixture was heated up to 70 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 1.26 mmol of n-butyl lithium (15% solution in cyclohexane) via pump within about 30 seconds. Then the polymerization started. The temperature in the reactor was kept constant at 70 °C. The reaction was finished after 90 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.95% was measured. The resulting polymer was analyzed by GPC: Mn=606718, Mw=761935, D=1.256. The microstructure and styrene block content were measured by ^{1}H-NMR. The following results were obtained: styrene=40.7%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=40%, block styrene having more than 4 styrene units=43%, and block styrene having more than 6 styrene units=7%.

[0079] **EXAMPLE 7** (Use of K-3,7-dimethyl-3-octylate (50% in hexanes) / DOP)

[0080] 18787 g of dried cyclohexane were charged into an airfree and nitrogen-purged, 40-liter, stainless steel reactor. 2343 g of 1,3-Butadiene, 929.56 g of styrene, 1.693 mmol of K-3,7-dimethyl-3-octylate (50% in heptane), and 3.394 mmol DOP were fed into the reactor (K/active butyl lithium mol/mol=0.096, DOP/active butyl lithium mo/mol=0.192). The mixture was heated up to 65 °C with stirring. The impurities in the system were titrated by stepwise addition of butyllithium. Recognizing the endpoint the polymerization was started by addition of the total amount of 17.6 mmol of n-

butyl lithium (15% solution in cyclohexane) via nitrogen pressure within 5 seconds. Then the polymerization started. The temperature in the reactor was kept constant at 65 °C. The reaction was finished after 60 minutes by addition of methanol as stopping agent. Irganox 1520 was introduced as antioxidant. A sample was taken by mean of a sampling tube with a stopcock and a needle for determination of the solid content. A conversion of 99.67% was measured. The resulting polymer was analyzed by GPC: Mn=252670, Mw=275487, D=1.09. The microstructure and styrene block content were measured by 1H-NMR. The following results were obtained: styrene=28%, vinyl (1,2-polybutadiene, calculated on the butadiene fraction)=28.9%, block styrene having more than 4 styrene units=45%, and block styrene having more than 6 styrene units=10%.

[0081] The Examples and Comparative Examples demonstrate that the present teachings provide a styrene-butadiene copolymer with a defined target styrene content with more than 4 consecutive styrene units, in combination with a high overall styrene content, a desired vinyl content and a narrow molecular weight distribution. By using a process in accordance with the present teachings, the novel and inventive polymers as claimed herein can be polymerized using standard polymerization techniques in high yield. All properties of the polymers as disclosed herein are properties prior to any subsequent modification, such as end-capping, coupling etc. as described above. Due to the achievement of the present teachings to provide polymers with narrow molecular weight distribution, it is possible to obtain a high amount of living chain ends at the end of the polymerization, so that uniform chain end modification is made possible.

[0082] The entire contents of every one of the patent and non-patent documents cited above are hereby incorporated by reference, except that in the event of any inconsistent disclosure or definition from the present specification, the disclosure or definition herein shall be deemed to prevail.

[0083] The foregoing detailed description has been provided by way of explanation and illustration, and is not intended to limit the scope of the appended claims. Many variations in the presently preferred embodiments

illustrated herein will be apparent to one of ordinary skill in the art, and remain within the scope of the appended claims and their equivalents.

CLAIMS

1. A polymer having at least the following characteristics:

(a) a block styrene content with more than 4 consecutive styrene units from about 40 to about 70 weight percent based on total styrene content in the polymer;

(b) a vinyl content from about 25 to about 80 weight percent based on total amount of polymerized 1,3-diene;

(c) a styrene content from about 20 to about 75 weight percent based on total weight of polymer; and

(d) a molecular weight distribution (Mw/Mn) of 1.5 or less.

2. The polymer of claim 1 having a block styrene content with more than 6 consecutive styrene units of from about 5 to about 30 weight percent based on total styrene content in the polymer, preferably the polymer has a block styrene content with more than 6 consecutive styrene units of from about 19 to about 26 weight percent based on total styrene content in the polymer.

3. The polymer as in any of the preceding claims having a styrene content of between about 25 and about 65 weight percent based on total styrene content, preferably between about 50 and about 60.

4. The polymer as in any of the preceding claims having a molecular weight distribution (Mw/Mn) from about 1.05 to about 1.5, preferably from about 1.1 to about 1.4, more preferably from about 1.2 to about 1.4.

5. The polymer as in any of the preceding claims wherein the 1,3-diene comprises 1,3-butadiene.

6. The polymer as in any of the preceding claims having a number-average molecular weight (Mn) greater than or equal to about 200,000 g/mole, preferably greater than or equal to about 400,000 g/mole, and more preferably greater than or equal to about 550,000 g/mole and/or a weight-average molecular weight (Mw) greater than or equal to about 300,000 g/mole, preferably greater than or equal to about 500,000 g/mole, and more preferably greater than or equal to about 600,000 g/mole.

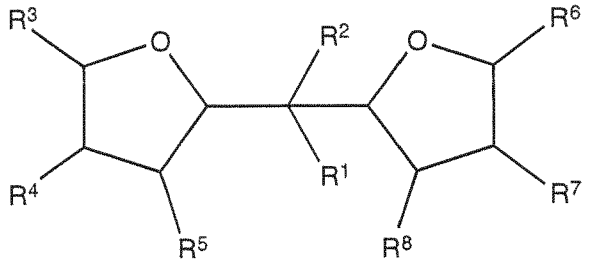
7. A composition comprising the polymer as in any of the preceding claims and optionally at least one additive.

8. An article comprising at least one component formed from the composition of claim 7.

9. A process for polymerization of a polymer comprising monomeric units derived from a styrene monomer and a 1,3-diene monomer, the process comprising:

polymerizing the monomeric units in the presence of an initiator such as n-butyllithium, a potassium alcoholate and a polar agent;

wherein the polar agent comprises a structure I:



(I);

wherein R^1 and R^2 are each independently an alkyl group;

wherein R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of an alkyl group and hydrogen.

10. The process of claim 9 wherein R^1 and R^2 are each independently a C_1-C_4 alkyl group, preferably methyl and/or R^3, R^4, R^5, R^6, R^7 and R^8 are each independently selected from the group consisting of hydrogen and a C_1-C_4 alkyl group.

11. The process as in any of claims 9 or 10 wherein the polar agent comprises ditetrahydrofurylpropane.

12. The process as in any of claims 9 to 11 wherein the potassium alcoholate comprises potassium-3,7-dimethyl-3-octylate.

13. The process as in any of claims 9 to 10 wherein the molar ratio of the potassium salt to active initiator is between about 0.05 and about 5, preferably between about 0.1 and about 1.

14. The process as in any of claims 9 to 13 wherein the polymerization is run at a temperature of about 80 °C or less, preferably between about 10 °C and about 80 °C, more preferably between 20 °C and 75 °C and/or the molar ratio of the polar agent to the potassium alcoholate is between about 30:1 and about 1:5, preferably between about 15:1 and 1:1.5 and/or the molar ratio of polar agent to active initiator is between about 0.1 and about 3, preferably between about 0.2 and about 1.5.

15. The process as in any of claims 9 to 14 wherein total monomer conversion is greater than about 96 weight percent based on total amount of monomer feed, preferably greater than about 98 weight percent, and more preferably greater than about 99 weight percent.

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/062095

A. CLASSIFICATION OF SUBJECT MATTER
INV. C08F236/10 C08F212/08 C08L9/06 C08L25/10
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08F C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 798 339 A2 (BRIDGESTONE CORP [JP]) 1 October 1997 (1997-10-01) cited in the application	1-11, 13-15
Y	abstract; example 1; tables 1-3 page 1, line 3 - line 10 page 3, line 11 - line 51 page 4, line 30 - page 5, line 6 -----	12
X	US 5 916 962 A (SHIBATA TADASHI [JP] ET AL) 29 June 1999 (1999-06-29) cited in the application column 4, line 9 - line 19; examples 1-8; table 2 column 5, line 20 - line 53 column 11, line 60 - line 63 ----- -/--	9-11, 13-15

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
27 August 2012	05/09/2012

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Mettler, Rolf-Martin

1

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2012/062095

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 698 646 A (KITAMURA TAKASHI [US] ET AL) 16 December 1997 (1997-12-16) * samples B, C, D *; example 1; table III column 10, line 1 - line 4 -----	9-11, 13-15
Y	US 6 521 712 B1 (KNOLL KONRAD [DE] ET AL) 18 February 2003 (2003-02-18) cited in the application column 2, line 52 - line 67; examples -----	12

1

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2012/062095

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0798339 A2	01-10-1997	DE 69712962 D1	11-07-2002
		DE 69712962 T2	14-11-2002
		EP 0798339 A2	01-10-1997
		ES 2174183 T3	01-11-2002
		US 6472464 B1	29-10-2002
US 5916962 A	29-06-1999	DE 69312891 D1	11-09-1997
		DE 69312891 T2	08-01-1998
		EP 0603886 A1	29-06-1994
		JP 3319639 B2	03-09-2002
		JP 6239909 A	30-08-1994
		US 5550200 A	27-08-1996
		US 5916962 A	29-06-1999
US 5698646 A	16-12-1997	DE 69411984 D1	03-09-1998
		DE 69411984 T2	10-12-1998
		EP 0622381 A1	02-11-1994
		ES 2119008 T3	01-10-1998
		JP 7002916 A	06-01-1995
		US 5698646 A	16-12-1997
US 6521712 B1	18-02-2003	AT 342293 T	15-11-2006
		AT 405598 T	15-09-2008
		AU 3431300 A	16-10-2000
		BR 0009361 A	26-12-2001
		CA 2368312 A1	05-10-2000
		CN 1345343 A	17-04-2002
		CZ 20013391 A3	12-12-2001
		DE 19914075 A1	28-09-2000
		EP 1171497 A1	16-01-2002
		EP 1690879 A1	16-08-2006
		ES 2274780 T3	01-06-2007
		ES 2311266 T3	01-02-2009
		HU 0201377 A2	28-08-2002
		JP 3976505 B2	19-09-2007
		JP 2002540268 A	26-11-2002
		JP 2004231975 A	19-08-2004
		KR 20010110695 A	13-12-2001
		MX 222345 B	27-08-2004
		PL 350996 A1	24-02-2003
		UA 72512 C2	15-03-2005
		US 6521712 B1	18-02-2003
		WO 0058380 A1	05-10-2000