



(51) International Patent Classification:

C07C 13/32 (2006.01)

C07C 23/18 (2006.01)

C07C 13/44 (2006.01)

(21) International Application Number:

PCT/US2018/042636

(22) International Filing Date:

18 July 2018 (18.07.2018)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/533,706

18 July 2017 (18.07.2017)

US

(71) Applicant (for all designated States except US): **THE UNIVERSITY OF AKRON** [US/US]; 302 E. Buchtel Common, Akron, Ohio 44325 (US).

(72) Inventors; and

(71) Applicants (for US only): **KENNEDY, Joseph** [US/US]; 510 St. Andrews Drive, Akron, Ohio 44303 (US). **NUGAY, Turgut** [TR/TR]; c/o Bogazici University Department of Chemistry, 34342 Istanbul (TR). **NUGAY, Nihan** [TR/TR]; c/o Bogazici University Department of Chemistry, 34342 Istanbul (TR).

(74) Agent: **SKOGLUND, Rodney** et al.; 106 South Main Street, First National Tower, Suite 400, Akron, Ohio 44308 (US).

(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, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, 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, ST, 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, KM, ML, MR, NE, SN, TD, TG).

Published:

— with international search report (Art. 21(3))

(54) Title: HIGH-STRENGTH LOW-CREEP THERMOPLASTIC ELASTOMER



Fig. 1

(57) Abstract: A polystyrene-g-(polyisobutylene-b-polystyrene) is taught. The polystyrene-g-(polyisobutylene-b-polystyrene) is synthesized by first providing a polystyrene backbone. Once the polystyrene backbone is provided, the polystyrene backbone is acetylated to provide acetyl groups on the polystyrene backbone. Next, the acetyl groups are converted to $-C(CH_3)_2OH$ groups. Finally, the living polymerization of isobutylene is initiated, which is then followed by the living block polymerization of styrene. A polymer network of polystyrene-g-(polyisobutylene-b-polystyrene)s is also provided.



HIGH-STRENGTH LOW-CREEP THERMOPLASTIC ELASTOMER**CROSS-REFERENCE TO RELATED APPLICATIONS**

5 **[0001]** This application claims the benefit of U.S. Provisional Application Serial No. 62/533,706 entitled “Graft SIBS: A New High-Strength Low-Creep Thermoplastic Elastomer” filed July 18, 2017, which is incorporated herein by reference in its entirety.

FIELD OF THE INVENTION

10 **[0002]** The present invention relates to a novel thermoplastic elastomer. More particularly, the present invention relates to a novel thermoplastic elastomer exhibiting advantageous mechanical properties such as high strength and very low creep. Specifically, the present invention relates to the structure and synthesis of a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) (PSt-*g*-P(IB-*b*-St)), wherein the living
15 cationic polymerization of isobutylene may be initiated by various one or more functionalized polystyrene backbones at various sites along the at least one polystyrene backbone. The resulting structure provides for two or more polyisobutylenes grafted to any one polystyrene backbone, wherein styrene can then be polymerized after the isobutylene, so as to provide a PSt-*g*-P(IB-*b*-St) as defined
20 herein exhibiting advantageous mechanical properties such as, amongst others, high-strength and very low creep. The present invention also relates to polymer networks of PSt-*g*-P(IB-*b*-St).

BACKGROUND OF THE INVENTION

25 **[0003]** Poly(Styrene-*b*-Isobutylene-*b*-Styrene) (SIBS) is a thermoplastic elastomer that has gained attention recently due to its high degree of biocompatibility. Due to its biocompatibility, SIBS has been found to be useful for a variety of application, such as stent coating, stoppers, glaucoma shunt, and tubing. This linear block copolymer has a triblock structure formed by a polyisobutylene (PIB) core sandwiched between
30 blocks of polystyrene (PS). The formulation of SIBS can be tailored for different

applications by changing the weight percentage of PS or by changing the molecular weight of the polymer chains. The hard PS blocks provide SIBS with a glassy microstructure that enhances mechanical strength and rigidity of the material, while the PIB has a soft microstructure with increased chain mobility that gives the polymer its elastomeric properties. The possibility of tailoring mechanical properties, together with the high degree of biocompatibility, makes SIBS an ideal material for use in biomedical devices.

[0004] However, there is a high cost associated with making SIBS. The high cost (30-40%) of most SIBS products is largely due to the expensive bifunctional polymerization initiator need for synthesis. Typically, that expensive bifunctional polymerization initiator is 1-(tert-butyl)-3,5-bis(2-chloropropan-2-yl)benzene. A commercial version of SIBS, named SIBSTAR, available from Kaneka Co., used mainly as additive in various industrial applications, is strongly contaminated with ill-defined diblocks.

[0005] Block copolymers of similar compositions might have diverse mechanical properties due to their composite nature. Parameters such as molecular weight, block weight percentage, and polymer chain structure are known to give rise to different microstructures that in turn lead to different material properties. Different grades of SIBS can have very different morphologies based on the ratio of hard phase to soft phase. At lower contents of PS, the hard phase forms spherical domains through the soft matrix. As the PS content increases, the spherical domains become double gyroid structures, and as the PS content is further increased, the structure of the hard phase becomes lamellar. It is likely that the incompatibility of the soft and hard phases leads to micro-phase separations and results in the different morphologies described. It is well known that for composite systems, the interface between different phases plays a major role in the performance of the material. A weakened interface might lead to premature cracking and failure. Additionally, the method of fabrication for SIBS might play a very important role due to the incompatibility of the different phases. Therefore, different methods may result in different qualities of the interface.

[0006] However, for all of its attributes, SIBS has been found to be of modest strength and tends to exhibit high creep. Therefore, the need exists for a new material, useful for implantable medical devices and industrial applications, that has the key advantageous properties of SIBS, such as biocompatibility, biostability, elasticity, and processability, but that also exhibits higher strength, toughness, and diminished creep, which SIBS does not exhibit. Furthermore, this new material should be able to be synthesized without the use of a costly multi-functional initiator.

SUMMARY OF THE INVENTION

[0007] In one embodiment, the present invention provides a polystyrene-g-(polyisobutylene-*b*-polystyrene). Said another way, the present invention provides a polymer composition having a polystyrene backbone and at least two polyisobutylene-polystyrene block copolymers grafted to the polystyrene backbone.

[0008] In another embodiment, the present invention provides the polystyrene-g-(polyisobutylene-*b*-polystyrene) in the embodiment above, wherein the graft-block copolymer has a tensile strength of greater than 20 MPa.

[0009] In another embodiment, the present invention provides a polystyrene-g-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the graft-block copolymer has an elongation of greater than 400%.

[0010] In a further embodiment, the present invention provides a method of synthesizing a polystyrene-g-(polyisobutylene-*b*-polystyrene) comprising the steps of providing a polystyrene backbone; acetylating the polystyrene backbone to provide between about 2 and about 20 acetyl groups on the polystyrene backbone; converting the acetyl groups to -C(CH₃)₂OH groups; and initiating in the presence of a co-initiator the living block polymerizations of isobutylene followed by styrene. More particularly, the living block polymerizations may be the living cationic polymerization of isobutylene followed by the living cationic polymerization of styrene.

[0011] In a related embodiment, the present invention provides a method of synthesizing a polystyrene-g-(polyisobutylene-*b*-polystyrene) as in any embodiment

above, wherein the step of acetylating provides between 3 and 7 acetyl groups and preferably 4 and 7 acetyl groups, on the polystyrene backbone.

[0012] In another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment
5 above, wherein the step of acetylating provides 5 or 6 acetyl groups on the polystyrene backbone.

[0013] In yet another embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein prior to the step of initiating, the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups are converted
10 to $-\text{C}(\text{CH}_3)_2\text{Cl}$ groups.

[0014] In another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the step of converting the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{Cl}$ groups uses hydrogen chloride to convert the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{Cl}$ groups.

[0015] In still another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein prior to the step of initiating, the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups are converted to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups.

[0016] In yet another related embodiment, the present invention provides a
20 method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the step of converting the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups uses sodium hydride and methyl iodide to convert the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups.

[0017] In another related embodiment, the present invention provides a method
25 of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the co-initiator is TiCl_4 .

[0018] In a further related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment

above, wherein the polymerization is terminated by methanol so as to precipitate the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) and to decompose the TiCl_4 .

[0019] In a further embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment
5 above, wherein the molecular weight of the polystyrene backbone is from about 5,000 g/mol to about 50,000 g/mol.

[0020] In still another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the method produces a polystyrene-*g*-(polyisobutylene-*b*-
10 polystyrene) having multiple polyisobutylene branch segments, and wherein the molecular weight of each of the multiple polyisobutylene branch segments is from about 10,000 g/mol to about 60,000 g/mol.

[0021] In another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment
15 above, wherein the method produces a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) having multiple polystyrene branch segments, and wherein the molecular weight of each of the multiple polystyrene branch segments is from about 5,000 g/mol to about 50,000 g/mol.

[0022] In another related embodiment, the present invention provides a method
20 of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the step of acetylating uses acetyl chloride in the presence of aluminum chloride, and wherein methylene chloride is a solvent to provide para-acetyl groups on the polystyrene backbone.

[0023] In yet another related embodiment, the present invention provides a
25 method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any embodiment above, wherein the step of converting the acetylated groups first uses methyl magnesium bromide, and then water or tetrahydrofuran to convert the acetylated groups to $-\text{C}(\text{CH}_3)_2\text{OH}$ groups.

[0024] In still another related embodiment, the present invention provides a
30 method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any

embodiment above, wherein the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) synthesized has a tensile strength of greater than 20 MPa.

[0025] In yet another related embodiment, the present invention provides a method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) as in any
5 embodiment above, wherein the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) synthesized has an elongation of greater than 400%.

[0026] In another embodiment, the present invention provides a polymer network of polystyrene-*g*-(polyisobutylene-*b*-polystyrene).

[0027] In a further related embodiment, the present invention provides a polymer
10 network as in any embodiment above, wherein each polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the polymer network contains a polystyrene backbone, multiple polystyrene branch segments, and multiple polyisobutylene branch segments.

[0028] In yet a further related embodiment, the present invention provides a polymer network as in any embodiment above, wherein each polystyrene branch
15 segment of each polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the network aggregate towards other polystyrene branch segments of other polystyrene-*g*-(polyisobutylene-*b*-polystyrene)s.

[0029] In still a further related embodiment, the present invention provides a polymer network as in any embodiment above, wherein the polyisobutylene branch
20 segments of each polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the network prevent aggregation of the polystyrene backbones of each polystyrene-*g*-(polyisobutylene-*b*-polystyrene).

[0030] In a further embodiment, the present invention provides an initiator for the polymerization of isobutylene, wherein the initiator is a functionalized polystyrene
25 wherein the functionalized polystyrene has reactive groups selected from the group consisting of -OH, -Cl, or -OMe groups functionalized and extending from at least two benzene rings of the polystyrene backbone. More particularly, the reactive groups extend from the para position on the benzene rings. In another embodiment, the reactive groups extend from no more than about 20 benzene rings of the polystyrene
30 backbone.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures in which:

[0032] Fig 1 is a representative structural formula of a PSt-g-P(IB-*b*-St); and

[0033] Fig. 2 is a representative microarchitecture of a representative PSt-g-P(IB-*b*-St)₅ polymer network.

DETAILED DESCRIPTION OF ILLUSTRATIVE EMBODIMENTS

[0034] The present invention generally relates to a novel thermoplastic elastomer having improved mechanical properties over ordinary thermoplastic elastomers. It will be appreciated that the generally recognized understanding of the term “thermoplastic elastomer” refers to the class of copolymers or a physical mix of polymers (usually a plastic and a rubber) which consist of materials with both thermoplastic and elastomeric properties. Thermoplastic elastomers typically show advantages typical of both rubbery materials and plastic materials.

[0035] The novel thermoplastic elastomer of the present invention is a polystyrene-g-(polyisobutylene-*b*-polystyrene) (PSt-g-P(IB-*b*-St)). Polystyrene-g-(polyisobutylene-*b*-polystyrene) is defined as a polymer composition comprising a polystyrene backbone and at least two, (and less than about 20 per 5000 g/mol polystyrene backbone) polyisobutylene-polystyrene block copolymers grafted to the polystyrene backbone at at least two (and up to about 20 per 5000 g/mol polystyrene backbone) of the benzene rings of the polystyrene backbone. The polyisobutylene-*b*-polystyrene copolymers are not present at the end of the polystyrene backbone chain, but rather are grafted within the polystyrene backbone, or more specifically, are connected two or more of the benzene rings of the polystyrene backbone. It will be appreciated that two or more of the benzene ring structures of the polystyrene backbone have previously been functionalized with a -OH, -Cl or -OMe group,

preferably at the para position on the benzene ring structures, so as to enable the initiation of living cationic polymerization of isobutylene, when in the presence of a co-initiator. Subsequently, styrene can then be polymerized after the isobutylene, so as to provide the polyisobutylene-polystyrene block copolymer moiety. The resulting structure provides for two or more polyisobutylenes (and subsequently, two or more polyisobutylene-*b*-polystyrene(s),) grafted to any one polystyrene backbone.

[0036] It has been found that the novel PSt-g-P(IB-*b*-St) of the present invention exhibits advantageous mechanical properties such as, amongst others, high-strength and very low creep. Inasmuch as the thermoplastic elastomer itself is novel, the synthesis of the PSt-g-P(IB-*b*-St) is also novel in that it produces a thermoplastic elastomer exhibiting advantageous mechanical properties such as, amongst others, high-strength and very low creep. An additional important feature of the synthesis of the PSt-g-P(IB-*b*-St) is that the synthesis does not require the use of a costly bifunctional initiator, such as 1-(tert-butyl)-3,5-bis(2-chloropropan-2-yl)benzene. Instead, the synthesis of the PSt-g-P(IB-*b*-St) utilizes a functionalized polystyrene having either an -OH, -Cl, or -OMe group extending from at least two of the benzene rings of the functionalized polystyrene.

[0037] When the term “high-strength” is used in the context of the present invention, it can be defined as a material having a tensile strength of greater than 20 MPa, or, an elongation, as defined on a stress-strain curve, of greater than 400%, and more preferably, greater than 600% strain, as determined by ASTM D638 - Plastic Tensile Strength Test. It will be appreciated that SIBS does not have such a high tensile strength or elongation, in that SIBS is well known to have tensile strength below 20 MPa, and elongation less than 400% as determined by the same ASTM standards.

[0038] When the term “very low creep” is used in the context of the present invention, it can be defined as a material having less than 0.2% creep as determined by ASTM D2990-77 - Standard Test Method for Tensile, Compressive and Flexural Creep and Creep Rupture of Plastics. It will be appreciated that SIBS is well known to

have poor creep properties, in that SIBS is well known to have creep well above at least 0.5%, and higher as determined by the same ASTM standard.

[0039] As stated above, the synthesis of the PSt-g-P(IB-*b*-St) of the present invention does not require the use of an expensive initiator to initiate, or start, polymerization. Instead, the present invention utilizes a functionalized polystyrene as the initiator for the polymerization of isobutylene. In one or more embodiments of the present invention, the functionalized polystyrene used as the initiator for the polymerization of isobutylene contains -OH, -Cl, or -OMe terminal groups. In one or more embodiments of the present invention, the initiation takes place in the presence of a co-initiator. As defined within the context of the present invention, a co-initiator differs from a typical initiator in that a co-initiator will get eliminated, or washed away, from the final product and will leave behind no residue. The use of a functionalized polystyrene as an initiator and the use of a co-initiator in the synthesis of the present invention is an important feature in producing PSt-g-P(IB-*b*-St) because it improves the overall processability of the PSt-g-P(IB-*b*-St) as compared to the processability of SIBS., and at a much lower cost. In at least one embodiment, the polymerization that is initiated is the living cationic polymerization of the isobutylene followed by the living cationic polymerization of styrene.

[0040] In one embodiment of the present invention, the following synthesis route is taken to arrive at the novel thermoplastic elastomer, PSt-g-P(IB-*b*-St), of the present invention. To begin, a polystyrene backbone is provided. Then, the polystyrene backbone is acetylated so as to provide acetyl groups on the polystyrene backbone. Once the acetyl groups are provided on the polystyrene backbone, the acetyl groups are then converted to -C(CH₃)₂OH groups. Finally, living block polymerization of isobutylene followed by styrene is initiated utilizing a functionalized polystyrene in the presence of a co-initiator to create the novel thermoplastic elastomer PSt-g-P(IB-*b*-St) of the present invention.

[0041] In one embodiment of the present invention, the polystyrene backbone is acetylated by the use of acetyl chloride in the presence of aluminum chloride, and wherein methylene chloride is used as a solvent so as to provide acetyl groups on the

polystyrene backbone. In one or more embodiments, the acetyl groups provided on the polystyrene backbone are para-acetyl groups.

[0042] In one embodiment of the present invention, the step of converting the acetyl groups first uses methyl magnesium bromide, and then water to convert the acetyl groups to $-C(CH_3)_2OH$ groups. In another embodiment, the step of converting the acetyl groups first uses methyl magnesium bromide, and then tetrahydrofuran to convert the acetyl groups to $-C(CH_3)_2OH$ groups.

[0043] In one embodiment of the present invention, after the step of converting the acetyl groups to $-C(CH_3)_2OH$ groups, the $-C(CH_3)_2OH$ groups are then converted to $-C(CH_3)_2Cl$ groups using hydrogen chloride to convert the $-C(CH_3)_2OH$ groups to $-C(CH_3)_2Cl$ groups. In yet another embodiment of the present invention, after the step of converting the acetyl groups to $-C(CH_3)_2OH$ groups, the $-C(CH_3)_2OH$ groups are then converted to $-C(CH_3)_2OMe$ groups using sodium hydride and methyl iodide to convert the $-C(CH_3)_2OH$ groups to $-C(CH_3)_2OMe$ groups.

[0044] In one or more embodiments of the present invention, regardless of whether the acetyl groups have been converted to $-C(CH_3)_2OH$ groups, $-C(CH_3)_2Cl$ groups, or $-C(CH_3)_2OMe$ groups, the living block polymerization is initiated using the functionalized polystyrene and is coinitiated using titanium chloride and the polymerization is terminated by methanol so as to precipitate the novel thermoplastic elastomer PSt-g-P(IB-*b*-St) of the present invention and to decompose the remaining titanium chloride co-initiator.

[0045] Fig. 1 shows the structural formula of the novel thermoplastic elastomer PSt-g-P(IB-*b*-St) of one or more embodiments of the present invention. In one or more embodiments, the molecular weight of the polystyrene backbone of the novel thermoplastic elastomer is from about 5,000 g/mol to about 50,000 g/mol; the molecular weight of the polyisobutylene branches of the novel thermoplastic elastomer are from about 10,000 g/mol to about 60,000 g/mol; and the molecular weight of the polystyrene branches are from about 5,000 g/mol to about 50,000 g/mol. In one embodiment, the molecular weight of the polystyrene backbone of the

novel thermoplastic elastomer is about 13,000 g/mol; the molecular weight of the polyisobutylene branches of the novel thermoplastic elastomer are about 30,000 g/mol; and the molecular weight of the polystyrene branches are about 13,000 g/mol.

[0046] The molecular weights and their distribution of both the polystyrene and polyisobutylene segments can be precisely controlled by living cationic polymerization. In one or more embodiments of the present invention, it is believed that the superior combination of thermoplastic properties is obtained with a hard (polystyrene) /soft (polyisobutylene) segment ratio of from about 30/70 wt. % to about 40/60 wt. %. For example, with a targeted 30/70 wt. % hard/soft segment ratio, the molecular weight of the polystyrene segment should be between about 13,000 and 14,000 g/mol so as to obtain the maximum T_g (~100 °C) for the hard segment, and the molecular weight of the soft polyisobutylene segments should be about 30,000 g/mol. The morphology with either 30/70 wt.% hard/soft segment, or 40/60 wt.% hard/soft segment is expected to be spherical.

[0047] In one or more embodiments of the present invention, the molecular weights of both the polystyrene backbone and the polystyrene branch segments should be the same. The similarity in molecular weights is believed to give the desirable micromorphology of the elastomer of the present invention.

[0048] Fig. 2 shows the unique microarchitecture of a polymer network of PSt-g-P(IB-*b*-St) of the present invention. Each PSt-g-P(IB-*b*-St) of the network contains a rigid glassy segment carrying several rubbery-glassy segments. More particularly, each PSt-g-P(IB-*b*-St) in the polymer network contains a polystyrene backbone, multiple polystyrene branches, and multiple polyisobutylene branches.

[0049] The polyisobutylene branches largely prevent the aggregation of polystyrene backbones so that physical crosslinking will mainly involve unencumbered polystyrene branch segments. The physical crosslinking, or aggregation thereof, of the polystyrene branch segments is believed to take place due to van der Waals forces between the polystyrene branch segments. This microarchitecture, also commonly known as a polymer network, constrains extensibility but leads to multiple entanglements and better stress distribution, which result in superior strength and the

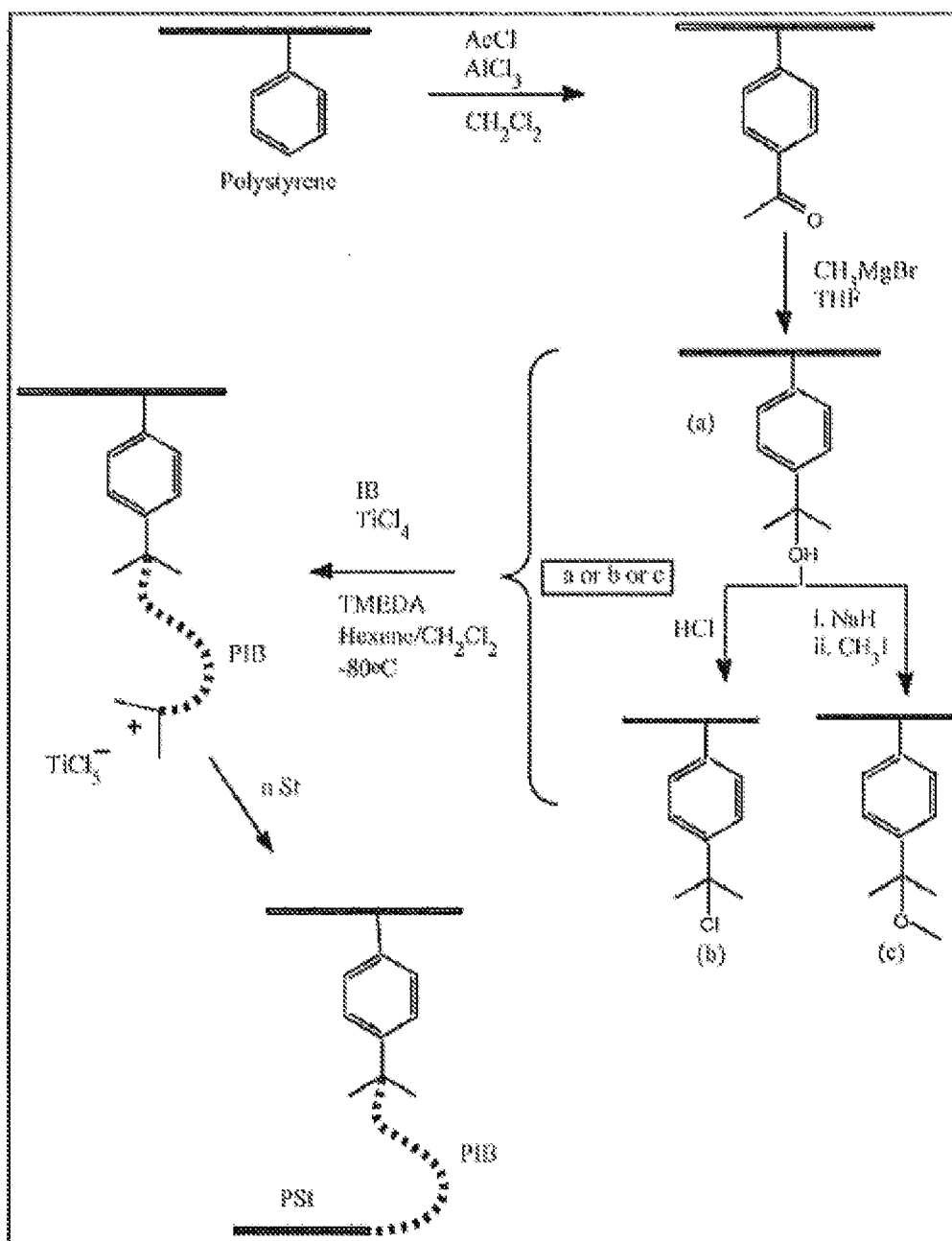
virtual absence of creep. Due to branching, the size of the ordered polystyrene domains tend to be small which is believed to lead towards improved stress transfer (strength), higher toughness, higher modulus, and lower viscosity.

Examples

5 **[0050]** In order to demonstrate practice of the invention, the following examples are offered to more fully illustrate the invention, but are not to be construed as limiting the scope thereof. Further, while some of examples may include conclusions about the way the invention may function, the inventors do not intend to be bound by those conclusions, but put them forth only as possible explanations. Moreover, unless
10 noted by use of past tense, presentation of an example does not imply that an experiment or procedure was, or was not, conducted, or that results were, or were not actually obtained. Efforts have been made to ensure accuracy with respect to numbers used (e.g., amounts, temperature), but some experimental errors and deviations may be present. Unless indicated otherwise, parts are parts by weight, molecular weight is
15 number average molecular weight, temperature is in degrees Centigrade, and pressure is at or near atmospheric.

[0051] The scheme below outlines the synthesis route taken to arrive at PSt-g-P(IB-*b*-St):

Scheme 1



[0052] Acetyl-chloride (AcCl), aluminum chloride (AlCl₃), magnesium sulfate (MgSO₄), titanium chloride (TiCl₄), styrene and polystyrene of Mn = 35,000 were obtained from Merck. Tetramethylethylene diamine (TMEDA) and methyl magnesium bromide (MeMgBr) solution were obtained from Sigma Aldrich and were used without further purification. Isobutylene (IB) was obtained from Exxon Mobile Co. Methylene chloride (CH₂Cl₂), tetrahydrofuran (THF) (or alternatively, water) and hexane (from TCI) were all distilled over calcium hydride prior to use.

[0053] The acetylated polystyrene (PS) starting material was prepared as follows: A 250 mL flask equipped with a 50mL addition funnel and a stir bar and containing anhydrous AlCl_3 (0.23 g, 1.7 mmol) was evacuated and protected by a blanket of gaseous N_2 . Then, 20 ml CH_2Cl_2 was then transferred into the flask via a capillary by
5 nitrogen pressure. The mixture was then cooled to 0°C , and AcCl (0.120 mL, 1.7 mmol) dissolved in 5 mL CH_2Cl_2 was then added dropwise from the addition funnel into the AlCl_3 solution during a 10 minute period. Then, polystyrene (10g, $M_n = 35,000$ g/mol, 0.20 mmol) dissolved in 100 mL of CH_2Cl_2 was added, and the reaction was then allowed to proceed for 15 minutes at room temperature. The
10 product obtained is then poured into a beaker containing approximately 10 of ice and 5 mL of concentrated HCl . Then, the inorganic layer formed is separated and washed successively with water and a 5% sodium bicarbonate solution. Once separated and washed, the inorganic layer is dried overnight over anhydrous MgSO_4 . A rotary evaporator then concentrated the solution and the product formed is precipitated into
15 excess methanol. The yield obtained was 10.07 g, which equates to approximately 99% acetylation.

[0054] The acetylated PS was characterized by ^1H NMR spectroscopy, which showed the expected structure, and GPC, which indicates that the M_n of the product did not change. This process introduces an estimated 6 acetyl groups per PS molecule,
20 i.e., the grafting density is 6.

[0055] The acetyl groups ($-\text{COCH}_3$) of the acetylated PS were converted to $-\text{C}(\text{CH}_3)_2\text{OH}$ groups (indicated as intermediate **a** in Scheme 1) as follows. 10.07 g of the acetylated PS was dissolved in 120 mL of anhydrous THF contained in a 500 mL round bottom flask. 1.2 mL of 3.0 M MeMgBr in diethyl ether is syringed dropwise
25 into the polymer solution under N_2 gas. After one hour, the reaction mixture was cooled to 0°C , and then 2 mL of 3 M HCl was added dropwise. The organic phase was then separated, washed with 20 mL of aqueous NaCl , dried over anhydrous CaCl_2 , concentrated by a rotary evaporator, and precipitated into excess methanol. The yield

obtained was approximately 10.10 g, which equates to approximately 99% completion of reaction.

[0056] The $-C(CH_3)_2OH$ groups are converted into $-C(CH_3)_2Cl$ groups (indicated as intermediate **b** in Scheme 1) as follows. Intermediate **a** (PSt with $-C(CH_3)_2OH$ groups, 10.10 g, 0.29 mmole) was placed in a Schlenk flask and dissolved in methylene chloride (100 mL) under a blanket of N_2 gas. The solution was then transferred by use of a stainless steel capillary into a flame dried 200 mL tubular reactor containing approximately 0.1 g $CaCl_2$. Gaseous HCl (generated by dropwise addition of sulfuric acid onto NaCl) was then bubbled into the solution using a Teflon capillary for six hours at $0^\circ C$ under a continuous nitrogen flush. The excess HCl was neutralized by absorbing the gas in aqueous sodium hydroxide. Then, the $CaCl_2$ was filtered off; the solution was concentrated by rotary evaporation; diluted with 100 mL of hexane; and washed with a solution of 5% aqueous sodium bicarbonate and water. The hexane layer was separated and then dried over $MgSO_4$. The drying agent was then filtered off and the solution was concentrated and precipitated in excess cold methanol. The resultant precipitate was separated by filtration, dried under vacuum at room temperature, and stored under nitrogen at $-20^\circ C$. The yield obtained was approximately 10.12 g, which equates to approximately 99% completion of reaction.

[0057] The $-C(CH_3)_2OH$ groups were converted into $-C(CH_3)_2OMe$ groups (indicated as intermediate **c** in Scheme 1) as follows. Intermediate **a** (PSt with $-C(CH_3)_2OH$ groups, 10.10 g, 0.29 mmole) was placed in a Schlenk flask and dissolved in THF (100 mL) under a blanket of N_2 gas. Then, NaH (0.082 g, 3.4 mmol) dissolved in 20 mL of THF was added dropwise for one hour at $0^\circ C$ under a nitrogen atmosphere. Next, CH_3I (0.32 mL, 5.1 mmol) dissolved in 10 mL of dried THF was added dropwise at $0^\circ C$. The solution was then stirred for 2 hours at $25^\circ C$, concentrated by a rotary evaporator, and precipitated into excess methanol. The yield obtained was approximately 10.11 g, which equates to approximately 99% completion of the reaction.

[0058] If beginning with intermediate **a**, (PSt with - C(CH₃)₂OH groups), the final steps of living block polymerization of isobutylene followed by styrene will be carried out first with the addition of isobutylene in the presence of a co-initiator such as TiCl₄. Subsequently, once the polymerization of the isobutylene has been completed, styrene will be added to the active polymer solution. Once the polymerization of the styrene has been completed, the polymerization will be terminated, the polymer will be washed and then dried; all solvents will then be removed and the final product, PSt-g-P(IB-*b*-St), will be collected.

[0059] When beginning with intermediate **b**, (PSt with - C(CH₃)₂Cl groups), the final steps of living block polymerization of isobutylene followed by styrene is carried out as follows. 1.5 g (0.043 mmol) of intermediate **b** was placed into a 500 mL round bottom flask equipped with a magnetic stir bar, the flask was evacuated and blanketed with N₂ gas. Next, 120 mL hexane and 80 mL of dichloromethane was added by a stainless steel capillary, and then TMEDA (0.078 mL, 0.52 mmol) was added by syringe under an N₂ atmosphere. The system was then cooled to -80° C. Then, IB (10.3 mL, 0.14 mol) was added, followed by the addition of TiCl₄ (0.29 mL, 2.61 mmol). The polymerization was allowed to proceed for one hour. Subsequently, styrene (4.31 mL, 37.6 mmol) was transferred into the active polymer solution. The polymerization of the added styrene was allowed to proceed for one hour and was terminated with the addition of 10 ml of methanol. The system was then warmed to room temperature, the solution was decanted, the polymer was dissolved in hexane, and then washed with 5% aqueous sodium bicarbonate and water. The organic phase was then dried overnight over magnesium sulfate, the solids were then removed by filtering through fine sintered glass. The solvent was removed by evaporation by use of a rotary evaporator. The product, PSt-g-P(IB-*b*-St), was then dried in a vacuum oven at 50° C for 2 days. The yield obtained was approximately 13.11 g, which equates to approximately 99% completion of reaction.

[0060] When beginning with intermediate **c**, (PSt with -C(CH₃)₂OMe groups), the final steps of living block polymerization of isobutylene followed by styrene is

carried out first with the addition of isobutylene in the presence of a co-initiator such as TiCl_4 . Subsequently, once the polymerization of the isobutylene has been completed, styrene will be added to the active polymer solution. Once the polymerization of the styrene has been completed, the polymerization will be terminated, the polymer will be washed and then dried; all solvents will then be removed and the final product, PSt-g-P(IB-*b*-St), will be collected.

[0061] Regardless of what intermediate is used, the final product of PSt-g-P(IB-*b*-St) can then be characterized by NMR spectroscopy, which will show the presence of both the PIB and PSt. The PSt-g-P(IB-*b*-St) created using intermediate **b**, as discussed above, showed high tensile strength elongation, toughness, and a low creep and the Inventors believe that PSt-g-P(IB-*b*-St) created using intermediate **a** or **c** will also show high tensile strength elongation, toughness, and a very low creep.

[0062] The same procedure as described above was repeated, except that the amount of styrene used during the final step of living block polymerization was increased. In this second example, the amount of styrene used was 5.7 mL (50.12 mmol) as compared to the 4.31 mL (37.6 mmol) used in the example above creating PSt-g-P(IB-*b*-St) using intermediate **b**. The composition and molecular architecture, respectively, of the two PSt-g-P(IB-*b*-St) formed are shown in Table 1 below.

Table 1

Example	Mn (g/mol) x 10 ⁻³				Composition (wt%)		
	PSt _{bb}	PIB _{br}	PSt _{br}	PSt-g-P(IB- <i>b</i> -St) ₆ **	PSt _{bb}	PIB _{br}	PSt _{br}
1	35	30	15	305	11.5	59.0	29.5
2	35	30	20	335	11.5	53.7	35.8

- bb in the subscript is backbone and br in the subscript is branch
- ** indicated the number of arms per PSt backbone

[0063] The PSt-g-P(IB-*b*-St) formed from Example 2 was characterized by NMR spectroscopy, which showed the presence of both the PIB and PSt. The PSt-g-P(IB-*b*-St) showed high tensile strength elongation, toughness, and a very low creep.

[0064] In light of the foregoing, it should be appreciated that the present
5 invention significantly advances the art by providing a novel structure and synthesis of a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) PSt-g-P(IB-*b*-St) that is structurally and functionally improved in a number of ways. While particular embodiments of the invention have been disclosed in detail herein, it should be appreciated that the invention is not limited thereto or thereby inasmuch as variations on the invention
10 herein will be readily appreciated by those of ordinary skill in the art. The scope of the invention shall be appreciated from the claims that follow.

CLAIMS

What is claimed is:

- 5 1. A polystyrene-*g*-(polyisobutylene-*b*-polystyrene).
2. The polystyrene-*g*-(polyisobutylene-*b*-polystyrene) of claim 1 having a tensile strength of greater than 20 MPa.
- 10 3. The polystyrene-*g*-(polyisobutylene-*b*-polystyrene) of claim 1 having an elongation of greater than 400%.
4. A method of synthesizing a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) comprising the steps of:
15 providing a polystyrene backbone;
 acetylating the polystyrene backbone to provide between about 2 and about 20 acetyl groups on the polystyrene backbone;
 converting the acetyl groups to -C(CH₃)₂OH groups; and
 initiating in the presence of a co-initiator the living block polymerizations of
20 isobutylene followed by styrene.
5. The method of claim 4, wherein the step of acetylating provides between 4 and 7 acetyl groups on the polystyrene backbone.
- 25 6. The method of claim 4, wherein the step of acetylating provides 5 or 6 acetyl groups on the polystyrene backbone.
7. The method of claim 4, wherein prior to the step of initiating, the -C(CH₃)₂OH groups are converted to -C(CH₃)₂Cl groups.

30

8. The method of claim 7, wherein the step of converting the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{Cl}$ groups uses hydrogen chloride to convert the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{Cl}$ groups.
- 5 9. The method of claim 4, wherein prior to the step of initiating, the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups are converted to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups.
- 10 10. The method of claim 9, wherein the step of converting the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups uses sodium hydride and methyl iodide to convert the $-\text{C}(\text{CH}_3)_2\text{OH}$ groups to $-\text{C}(\text{CH}_3)_2\text{OMe}$ groups.
11. The method of claim 4, wherein the co-initiator is TiCl_4 .
- 15 12. The method of claim 11, wherein the polymerization is terminated by methanol so as to precipitate the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) and to decompose the TiCl_4 .
- 20 13. The method of claim 4, wherein the molecular weight of the polystyrene backbone is from about 5,000 g/mol to about 50,000 g/mol.
- 25 14. The method of claim 4, wherein the method produces a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) having multiple polyisobutylene branch segments, and wherein the molecular weight of each of the multiple polyisobutylene branch segments is from about 10,000 g/mol to about 60,000 g/mol.
- 30 15. The method of claim 4, wherein the method produces a polystyrene-*g*-(polyisobutylene-*b*-polystyrene) having multiple polystyrene branch segments, and wherein the molecular weight of each of the multiple polystyrene branch segments is from about 5,000 g/mol to about 50,000 g/mol.

16. The method of claim 4, wherein the step of acetylating uses acetyl chloride in the presence of aluminum chloride, and wherein methylene chloride is a solvent to provide para-acetyl groups on the polystyrene backbone.
- 5 17. The method of claim 16, wherein the step of converting the acetylated groups first uses methyl magnesium bromide, and then water or tetrahydrofuran to convert the acetylated groups to $-C(CH_3)_2OH$ groups.
- 10 18. The method of claim 4 wherein the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) synthesized has a tensile strength of greater than 20 MPa.
19. The method of claim 4 wherein the polystyrene-*g*-(polyisobutylene-*b*-polystyrene) synthesized has an elongation of greater than 400%.
- 15 20. A polymer network of polystyrene-*g*-(polyisobutylene-*b*-polystyrene).
21. The polymer network of claim 20 wherein each polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the network contains a polystyrene backbone, multiple polystyrene branch segments, and multiple polyisobutylene branch segments.
- 20 22. The polymer network of claim 21 wherein each polystyrene branch segment of polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the network aggregate towards other polystyrene branch segments of other polystyrene-*g*-(polyisobutylene-*b*-polystyrene)s.
- 25 23. The network of claim 22 wherein the polyisobutylene branch segments of each polystyrene-*g*-(polyisobutylene-*b*-polystyrene) in the network prevent aggregation of the polystyrene backbones of each polystyrene-*g*-(polyisobutylene-*b*-polystyrene).
- 30

24. An initiator for the polymerization of isobutylene, wherein the initiator is a functionalized polystyrene wherein the functionalized polystyrene has reactive groups selected from the group consisting of -OH, -Cl, or -OMe groups functionalized and extending from at least two benzene rings of the polystyrene backbone.
- 5

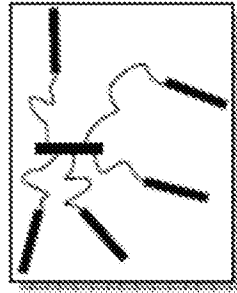


Fig. 1

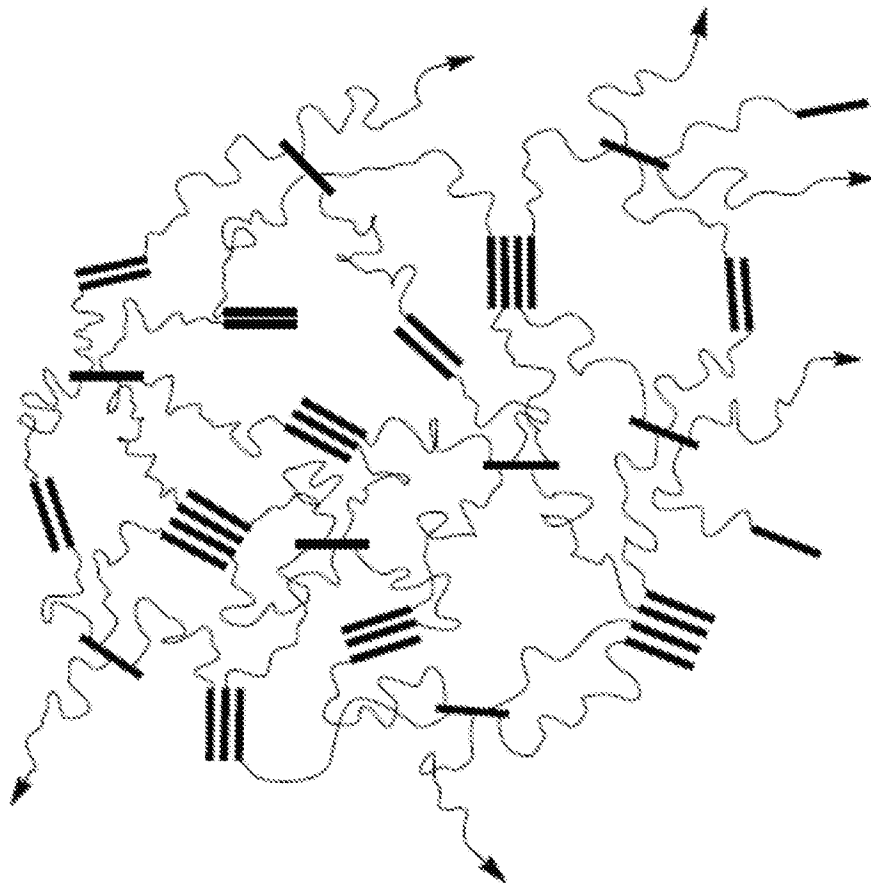


Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 18/42636

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - C07C 13/32, C07C 13/44, C07C 23/18 (2018.01)
 CPC - C07C 13/44, C07C 211/27, C07C 23/18

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)

See Search History Document

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

See Search History Document

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

See Search History Document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	Atta 'Graft copolymerization of polyisobutylene and polychlorobutyl onto polystyrene waste', Polymer International, 18 August 1999 (18.08.1999), Vol.48, pages837-842; p839	24
Y	US 6,512 056 B1 (Kennedy et al.) 28 January 2003 (28.01.2003); col5, col6	24
A	US 3,894,119 A (Forbes et al.) 08 July 1975 (08.07.1975); Abstract	1-23
A	Kali et al. 'A New Synthetic Method for the Preparation of Star-Shaped Polyisobutylene with Hyperbranched Polystyrene Core', Macromolecular Chemistry and Physics, 02 July 2007 (02.07.2007), Vol.208, pages1388-1393; p1390	1-23
A	US 2010/0076538 A1 (Desai et al.) 25 March 2010 (25.03.2010); para[0022]	1-3, 20-23
A	EP 0 348 963 A2 (Ceskoslovenska Akademie) 03 January 1990 (03.01.1990); p8	1-3, 20-23
A	Jankova et al. 'Synthesis of poly(styrene-b-isobutylene-b-styrene) triblock copolymer by ATRP', Polymer Bulletin, December 1998, Vol.41, pages639-644; Title	4-19

☐ Further documents are listed in the continuation of Box C.

☐ 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

10 October 2018

Date of mailing of the international search report

02 NOV 2018

Name and mailing address of the ISA/US

Mail Stop PCT, Attn: ISA/US, Commissioner for Patents
 P.O. Box 1450, Alexandria, Virginia 22313-1450

Facsimile No. 571-273-8300

Authorized officer:

Lee W. Young

PCT Helpdesk: 571-272-4300
 PCT OSP: 571-272-7774