(51) International Patent Classification: C08F 216/16 (2006.01)

(21) International Application Number: PCT/US20 13/0541 11

(22) International Filing Date: 8 August 2013 (08.08.2013)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data: 61/881,869 10 August 2012 (10.08.2012) US


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Published: with international search report (Art. 21(3)) [Continued on next page]

(54) Title: NOVEL POLYISOBUTYLENE-BASED THERMOPLASTIC ELASTOMERS

FIG. 1

(57) Abstract: The present invention is directed to a new class of thermoplastic elastomers (TPEs) and processes for making them. In some embodiments of the present invention, the end groups of the multi-arm PIB copolymer is a conjugated diene, whereas the other component is a multi-functional dieneophile. The components of the TPE of the present invention are chemically connected via the well-known Diels-Alder reaction which is thermally reversible (by the retro-Diels-Alder reaction) at moderately elevated temperatures. The reversibility of the Diels-Alder retro-Diels-Alder reactions allows the recovery of the original components of the TPE and thus its recyclability and also gives the TPE the ability to be reshaped or re-formed.
before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments (Rule 48.2(h))
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
   IPC(8) - C07C 41/14 (2014.01)
   USPC - 568/628

   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)
   IPC(8) - C07C 41/14, 43/166 (2014.01)
   USPC - 568/628, 663

   Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
   CPC - C07C 41/14, 43/166 (2014.02)

   Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
   PatBase, Orbit, PubChem, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, P</td>
<td>EP 2,495,262 A2 (PUSKAS) 05 September 2012 (05.09.2012) entire document</td>
<td>1.2</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:
  "A" document defining the general state of the art which is not considered to be of particular relevance
  "B" earlier application or patent 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
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  "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
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  "&" document member of the same patent family

Date of the actual completion of the international search: 10 April 2014

Date of mailing of the international search report: 17 APR 2014

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PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (July 2009)
This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.   □ Claims Nos.:  
      because they relate to subject matter not required to be searched by this Authority, namely:

2.   □ Claims Nos.:  
      because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3.   □ Claims Nos.:  
      because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

This International Searching Authority found multiple inventions in this international application, as follows:

See Extra Sheet

1.   □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2.   □ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3.   □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4.   □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

   1, 2

Remark on Protest

□ The additional search fees were accompanied by the applicant’s protest and, where applicable, the payment of a protest fee.

□ The additional search fees were accompanied by the applicant’s protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.
INTERNATIONAL SEARCH REPORT

<Continued from Box III: Observations where unity of invention is lacking>

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1 and 2 are drawn to a 3-(2-methoxyisopropyl)styrene composition having the formula (i), and methods of synthesis thereof.

Group II: Claims 3-11 are drawn to multi-arm polyisobutylene (PIB) polymers comprising: a) an oligomeric styrene prepolymer having a sec-butyl head group; and b) at least one PIB arm extending from each 3-(2-methoxoisopropyl)styrene.

Group III: Claims 12-34 are drawn to methods for synthesizing a multi-arm polyisobutylene having an oligomeric styrene, and a sec-butyl head group; and a thermoplastic elastomeric network thereof.

The first invention of Group II+ is restricted to a multi-arm polyisobutylene (PIB) polymer having one of formulas (vi) or (vii). In an exemplary election, the Formula vii compound is selected wherein n is 3, m is 3, and q is 10. It is believed that claims 3-5 read on this first exemplary election of Group II+. Applicant is invited to elect an exemplary election of formula (vi) or (vii) to be searched in a specific combination for each formula by paying additional fees for each election. Applicants must specify the claims that read on any additional elected inventions. Applicants must further indicate, if applicable, the claims which read on the first named invention if different than what was indicated above for this group. Failure to clearly identify how any paid additional invention fees are to be applied to the “+” group(s) will result in only the first claimed invention to be searched/examined.

The inventions listed in Groups I through III do not relate to a single general inventive concept under PCT Rule 13.2 because under PCT Rule 13.2 they lack the same or corresponding special technical features for the following reasons:

The special technical features of Group I, methods for synthesizing 3-(2-methoxoisopropyl)styrene, are not present in Groups II and III; the special technical features of Group II+, multi-arm polyisobutylene polymers, are not present in Groups I and III; and the special technical features of Group III, methods for synthesizing a multi-arm polyisobutylene having an oligomeric styrene, and a sec-butyl head group, are not present in Groups I and II+.

The Group II+ multi-arm polyisobutenyles do not share a significant structural element, requiring the selection of end groups selected from the group consisting of allyls, dienes, and furans.

The Groups I and II+ share the technical feature of a 3-(2-methoxoisopropyl)styrene moiety. However, these shared technical features do not represent a contribution over the prior art. Specifically, EP 2 495 262 A2 to Puskas teaches a 3-(2-methoxoisopropyl)styrene moiety (see Para. [0027], Exemplary inimers for use in conjunction with at least one isofuran to yield a polymer...-4-(2-methoxoisopropyl) styrene; Para. [0056], Scheme 1, see structure (IM)...).

The Groups II and III share the technical features of a multi-arm polyisobutylene (PIB) polymer comprising: an oligomeric styrene pre-polymer having a sec-butyl head group, a poly(a-methylstyrene) segment from about 3 to about 5 units in length and a poly [3-(2-methoxoisopropyl)styrene] segment, and at least one PIB arm extending from each 3-(2-methoxoisopropyl)styrene wherein said PIB arms are terminated with end groups selected from the group consisting of allyls, dienes, and furans. However, these shared technical features do not represent a contribution over the prior art.

Specifically, US 5,084,522 A to Frechet teaches a multi-arm polyisobutylene (PIB) polymer comprising: an oligomeric styrene pre-polymer having a sec-butyl styrene, and a poly [3-(2-methoxoisopropyl)styrene] segment, and at least one PIB arm extending from each 3-(2-methoxoisopropyl)styrene wherein said PIB arms are terminated with end groups selected from the group consisting of allyls (Col. 3 Lns. 49-62, a particularly preferred group of styrene derivatives of the invention are those compounds of the formula (shown); wherein R represents...methoxy...; Col. 4 Lns. 28-42, compounds of formula I can be copolymerized with styrene by standard free-radical polymerization techniques to produce copolymers containing both monomer units and having the formula (shown) III wherein R1, R2 and R3 are as defined above, x andy are integers from 1 to about 2000 and n is an integer from 1 to about 1000; Col. 9 Lns. 5-40, Example 10, Cationic graft copolymerization of isobutylene onto the copolymer of Example 6...in which each repeating unit contains approximately 49 unsaturated substituted styrene units for each substituted styrene unit to which is grafted a chain containing approximately 70 units of isobutylene...; where an unsubstituted terminal of the polyisobutylene branch would inherently consist of an allyl group).

Further, EP 2 495 262 A2 to Puskas teaches a multi-arm polyisobutylene (PIB) polymer comprising: an oligomeric styrene pre-polymer having a sec-butyl head group, and at least one PIB arm extending from each 3-(2-methoxoisopropyl)styrene wherein said PIB arms are terminated with end groups selected from the group consisting of dienes (Paras. [0020]-[0021], polymers for purification by the present invention can also include arborescent polymers formed from at least one inimer and at least one isofuran that have been end-functionalized with a low Tg homolog or copolymer that contains isoprene or any other cationically polymerizable monomer...polymers for purification by the present invention can also include arborescent polymers formed from at least one isofuran and at least one isofuran that have been end-functionalized with about 0.5 to about 5 weight percent end blocks derived from a diene or diene derivative...; Parases. [0095]-[0096], arPbIB-b-P(pMeSt)...; TICU (3.13 10-2 mol/L) into the reactor containing IB (240 mL, 1.74 mol/L), IM (2.28 10-3 mol/L) and DtBP (5.1 10-3 mol/L) as a proton trap in the solvent mixture (H2/McCl 60/40 v/v). After all IB reacts, a pre-chilled solution of 70 mL p-methylstyrene in 150 mL of MeCl and 250 mL of Hx, containing also 1.0 mL of DMA and 1 mL of DtBP is added...).

Since none of the special technical features of the Groups I through III inventions are found in more than one of the inventions, unity is lacking.

<End Box III: Observations where unity of invention is lacking>