BDSPs (*butadiene di-block stereoregular polymers*)

result of the joint research

ISMAC (*Giovanni Ricci, Giuseppe Leone*)/**Versalis** (*Francesco Masi, Anna Sommazzi, Salvatore Coppola*)

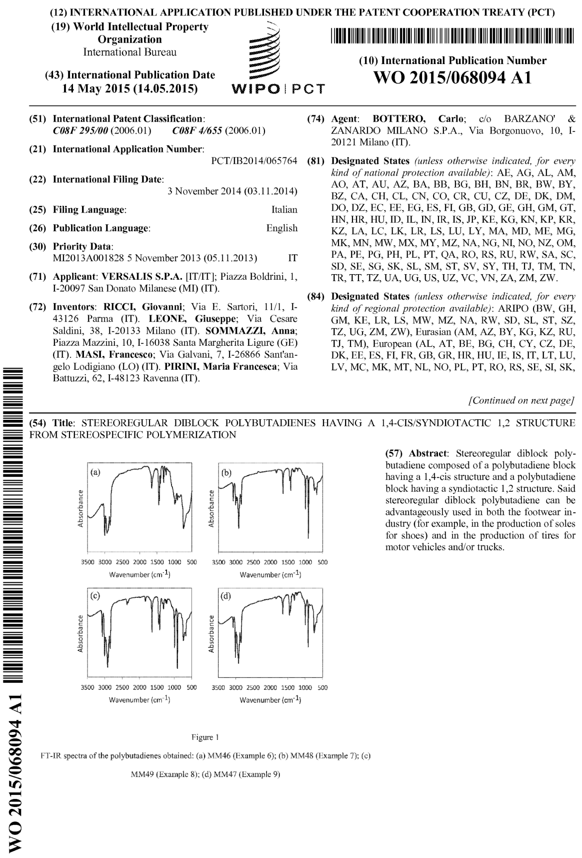
win the international award

TTI Award_ Tire Manufacturing Innovation of the Year

(http://www.tiretechnology-expo.com/en/awards.php)

In recognition of scientific and technological excellence in tire manufacturing

(https://www.youtube.com/watch?v=3VRWMqR2_Xg)


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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 May 2015 (14.05.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/068094 A1

(51) International Patent Classification: *C08F 295/00* (2006.01) *C08F 4/655* (2006.01)

(21) International Application Number: PCT/IB2014/065764

(22) International Filing Date: 3 November 2014 (03.11.2014)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data: MI2013A001828 5 November 2013 (05.11.2013) IT

(71) Applicant: **VERSALIS S.P.A.** [IT/IT]; Piazza Boldrini, 1, I-20097 San Donato Milanese (MI) (IT).

(72) Inventors: **RICCI, Giovanni**; Via E. Sartori, 11/1, I-43126 Parma (IT). **LEONE, Giuseppe**; Via Cesare Saldini, 38, I-20133 Milano (IT). **SOMMAZZI, Anna**; Piazza Mazzini, 10, I-16038 Santa Margherita Ligure (GE) (IT). **MASI, Francesco**; Via Galvani, 7, I-26866 Sant'angelo Lodigiano (LO) (IT). **PIRINI, Maria Francesca**; Via Battuzzi, 62, I-48123 Ravenna (IT).

(74) Agent: **BOTTERO, Carlo**; c/o BARZANO' & ZANARDO MILANO S.P.A., Via Borgonuovo, 10, I-20121 Milano (IT).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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,

[Continued on next page]

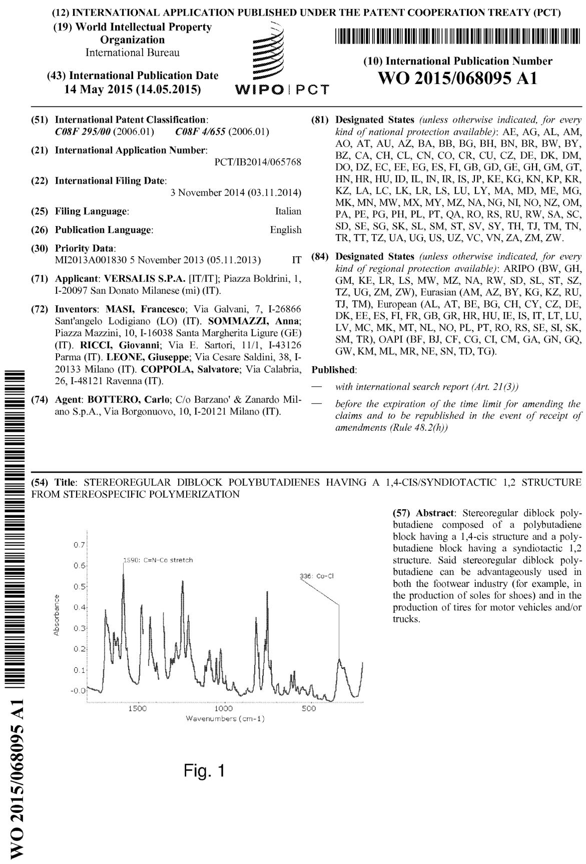
(54) Title: STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE FROM STEREOSPECIFIC POLYMERIZATION

(57) Abstract: Stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-cis structure and a polybutadiene block having a syndiotactic 1,2 structure. Said stereoregular diblock polybutadiene can be advantageously used in both the footwear industry (for example, in the production of soles for shoes) and in the production of tires for motor vehicles and/or trucks.

Figure 1

FT-IR spectra of the polybutadienes obtained: (a) MM46 (Example 6); (b) MM48 (Example 7); (c) MM49 (Example 8); (d) MM47 (Example 9)

WO 2015/068094 A1


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

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
14 May 2015 (14.05.2015)

WIPO | PCT

(10) International Publication Number
WO 2015/068095 A1

(51) International Patent Classification: *C08F 295/00* (2006.01) *C08F 4/655* (2006.01)

(21) International Application Number: PCT/IB2014/065768

(22) International Filing Date: 3 November 2014 (03.11.2014)

(25) Filing Language: Italian

(26) Publication Language: English

(30) Priority Data: MI2013A001830 5 November 2013 (05.11.2013) IT

(71) Applicant: **VERSALIS S.P.A.** [IT/IT]; Piazza Boldrini, 1, I-20097 San Donato Milanese (mi) (IT).

(72) Inventors: **MASI, Francesco**; Via Galvani, 7, I-26866 Sant'angelo Lodigiano (LO) (IT). **SOMMAZZI, Anna**; Piazza Mazzini, 10, I-16038 Santa Margherita Ligure (GE) (IT). **RICCI, Giovanni**; Via E. Sartori, 11/1, I-43126 Parma (IT). **LEONE, Giuseppe**; Via Cesare Saldini, 38, I-20133 Milano (IT). **COPPOLA, Salvatore**; Via Calabria, 26, I-48121 Ravenna (IT).

(74) Agent: **BOTTERO, Carlo**; C/o Barzano' & Zanardo Milano S.p.A., Via Borgonuovo, 10, I-20121 Milano (IT).

(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, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KN, KP, KR, 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))*

— *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))*

(54) Title: STEREOREGULAR DIBLOCK POLYBUTADIENES HAVING A 1,4-CIS/SYNDIOTACTIC 1,2 STRUCTURE FROM STEREOSPECIFIC POLYMERIZATION

(57) Abstract: Stereoregular diblock polybutadiene composed of a polybutadiene block having a 1,4-cis structure and a polybutadiene block having a syndiotactic 1,2 structure. Said stereoregular diblock polybutadiene can be advantageously used in both the footwear industry (for example, in the production of soles for shoes) and in the production of tires for motor vehicles and/or trucks.

Fig. 1

WO 2015/068095 A1

(da sx: Giuseppe Leone, Giovanni Ricci, Anna Sommazzi, Francesco Masi*)*

New butadiene based di-block stereoregular polymers for the development of innovative compounds - BDSPs.

A breakthrough technology to fill performance gaps on the BR marketplace

https://versalis.eni.com/irj/portal/anonymous?NavigationTarget=navurl://e36a2fce3c5df12e706329cbff9ad995&guest_user=anon_it

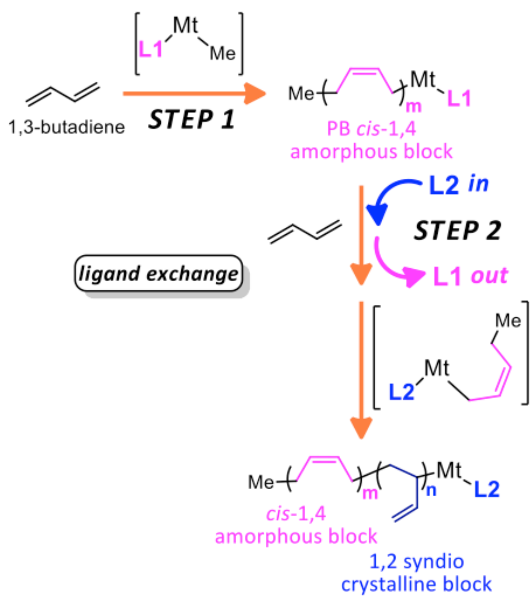
Versalis, in collaboration with **ISMAC-CNR**, has now developed a new generation of polybutadienes (**BDSPs**) showing the properties of a thermoplastic elastomer, *i.e.* the behavior of a viscoelastic liquid at processing and moulding temperatures, and elastomeric properties in application, without necessarily passing through a crosslinking process. This feature particularly applies in the tire production and most importantly allows recycling. It also brings advantage to many other applications requiring not-crosslinked elastomers, with considerable benefit for environmental sustainability.

Versalis **BDSPs** are a genuine breakthrough in the elastomers business with pioneering features regarding both catalysis and the stereoregular di-block polybutadienes.

Versalis **BDSPs** avail themselves of a specific polymerization catalysis which, having living character and high stereoselectivity, allows to obtain butadiene based stereoregular di-block polymers having *cis*-1,4/1,2 syndiotactic structure.

The *cis*-1,4 block is amorphous with low melting temperature (T_m) (well below room temperature), while the 1,2 syndiotactic block is crystalline with high T_m (above room temperature); the melting temperature of the crystalline block can be managed in the range 70° ÷ 140°C.

The 1,2 syndiotactic block, below its melting temperature, shows a filler-like behavior. Furthermore, the hard, phase separated, 1,2 syndiotactic block domains act as physical cross-links thus increasing the polymer elasticity.



Versalis **BDSPs** have been obtained through a new catalytic process involving the change of stereoselectivity of the catalytic centre during the living polymerization run.

The polymerization process involves the stereospecific polymerization of butadiene with catalysts based on cobalt organometallic complexes with suitable and original ligands L1 (STEP 1) giving a living, amorphous polybutadiene with *cis*-1,4 structure (≥ 97%). Then, after a variable polymerization time (t1), a different and original ligand L2 and further butadiene are added, determining a change in the selectivity of the living catalytic centre (STEP 2), with consequent formation of a crystalline 1,2 syndiotactic polybutadiene block. It is worthwhile to note that the two stereoregular polybutadiene blocks (amorphous *cis*-1,4 and crystalline syndiotactic 1,2) are linked through a single junction point.

The values of *m* and *n* (*i.e.*, the molecular weight of the two PB blocks, amorphous *cis*-1,4 and crystalline syndiotactic 1,2) depend on the amount of butadiene added in the two polymerization steps. The stereoregularity of the 1,2 polybutadiene block (*i.e.*, the percentage of syndiotactic triads [rr]), and indeed its melting temperature, depends on the type of L2 ligand used.

The innovative features of this new catalytic process enable to obtain ***a*)** high stereoregular di-block polybutadienes in which the two blocks have a single junction point, being the polymerization of a living type; ***b)*** to control the molecular weight of the two blocks, by varying the addition time of the ligand (L2) and/or the amount of butadiene in the feed; ***c)*** to control syndiotacticity degree of the 1,2-block, and its thermal properties (melting temperature, crystallization temperature and glass transition temperature) by appropriate choice of the type of ligand (L2).

The extreme versatility of the Versalis **BDSPs** innovative catalytic system, as highlighted in points *a-c* listed above, allows to modulate at will the features of the obtained stereoregular di-block polybutadienes.

Versalis new **BDSPs**, associated to the innovative catalysis developed for their preparation, allow to prepare compounds for applications in several fields such as tires, soles and technical articles, with improved properties compared to those nowadays available.

In particular, for instance, with the new compounds, it will be possible to develop tires usable both in summer and winter seasons, but with features at the top for both applications. Actually the "*all seasons*" tires have characteristics mediated between the winter and summer uses, and consequently with not optimal performances.

Versalis **BDSPs** featuring not cross-linked compounds could make the products obtained through this technology more easily recyclable and environmentally-friendly.

Moreover, considering that the **BDSPs** are based on an extremely new technology and that the two constituting blocks ("soft" amorphous block and "hard" crystalline block) are tunable at will as regards their molecular weight and length, type and degree of stereoregularity, thermal properties (melting temperatures, crystallization and glass transition), the potential applications of this new polymers go beyond tires and are all to discover and will open to a wide range of commercial segments, both in thermoplastic and elastomeric fields.