



(51) International Patent Classification:

B29C 64/124 (2017.01) *C08G 63/02* (2006.01)
A61L 27/58 (2006.01) *C08J 3/24* (2006.01)
A61L 31/14 (2006.01) *C08L 67/07* (2006.01)

(21) International Application Number:

PCT/US2020/043159

(22) International Filing Date:

23 July 2020 (23.07.2020)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

62/877,066 22 July 2019 (22.07.2019) US

(71) Applicant: **VENOSTENT, INC.** [US/US]; 1675 S State
 Street, Suite B, Dover, DE 19901 (US).

(72) Inventors; and

(71) Applicants (for US only): **BOIRE, Timothy C.** [US/US];
 2450 Holcombe Blvd, Suite J, Houston, TX 77021 (US).
MILLER, Jordan S. [US/US]; 2450 Holcombe Blvd,
 Suite J, Houston, TX 77021 (US). **GRIGORYAN, Bagrat**
 [US/US]; 2450 Holcombe Blvd, Suite J, Houston, TX
 77021 (US).

(74) Agent: **KILGORE, Mark**; Patterson Intellectual Property
 Law, P.C., 1600 Division Street, Suite 500, Nashville, TN
 37211 (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, IT, 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,

(54) Title: ADDITIVE MANUFACTURING OF VINYL, PHOTOCROSSLINKABLE POLYMERS

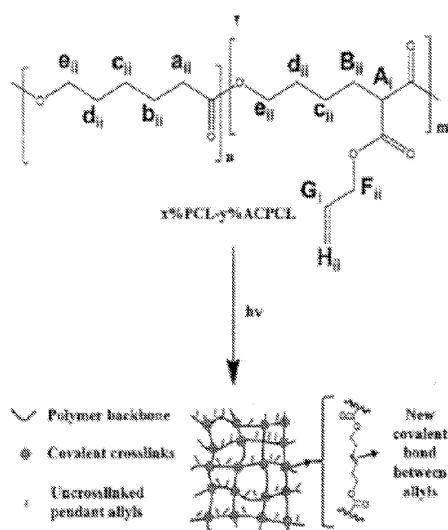


FIG. 1

(57) Abstract: Various precursor solutions and methods of 3D printing and other additive manufacturing approaches are provided for the manufacture of articles using photocrosslinkable vinyl shape memory polymers. In various aspects, articles are manufactured by a process comprising (i) exposing a precursor solution to an intensity and frequency of light to initiate photo-polymerization of the precursor solution to form a layer of the article; and (ii) repeating step (i) a number of times to form the article in a layer-by-layer approach; wherein the precursor solution comprises a first polymeric precursor comprising a plurality of vinyl terminated side-chains attached thereto. A vinyl-functionalized, photocrosslinkable SMP used as an example herein is a novel variant of a previously disclosed SMP composition, with higher amounts of vinyl functionalization but similar thermomechanical properties to the SMP library previously disclosed. Moreover, a unique combination of chemistries is disclosed that incorporates the aforementioned vinyl-functionalized SMPs along with acrylate-based crosslinkers. Additional novel compositions are disclosed containing the vinyl-functionalized SMPs with additional dithiol functionalizations, vinyl-functionalized SMPs with dithiol crosslinkers, as well as vinyl-functionalized SMPs with both acrylate-based and dithiol crosslinkers, as another means to tune degradation rates and other material properties. The articles can include a variety of articles such as stents, grafts, external sheaths, and the like. Beneficially, the printed articles can include a plurality of pores having an average diameter of about 50 pm to about 5000 pm, about 500 pm to about 2000 pm, or about 1000 pm even in the absence of a photoblocker.

[Continued on next page]

NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW,
SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN,
TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, 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))*
- *the filing date of the international application is within two months from the date of expiration of the priority period (Rule 26bis.3)*