Supporting Information

Synthesis of cross-linked polymeric microparticles containing hexa-O-benzylsucrose

Contents:

1',2,3,3',4,4'-Hexa-*O*-benzylsucrose (1) 2

    Figure S1.1. IR (NaCl) of 1 2

    Figure S1.2. ¹H NMR (CDCl₃, 400 MHz) of 1 3

    Figure S1.3. ¹³C NMR (CDCl₃, 100 MHz) of 1 4

1',2,3,3',4,4'-Hexa-*O*-benzyl-6,6'-di-*O*-methacryloylsucrose (2, new compound)..... 5

    Figure S2.1. IR (NaCl) of 2 5

    Figure S2.2. ¹H NMR (CDCl₃, 400 MHz) of 2 6

    Figure S2.3. ¹³C NMR (CDCl₃, 100 MHz) of 2 7

    Figure S2.4. DEPT of 2 8

    Figure S2.5. COSY of 2 9

    Figure S2.6. HMQC of 2 9

    Figure S2.7. MALDI-TOF of 2 10

6,6'- Di-*O*-allyl-1',2,3,3',4,4'-hexa-*O*-benzylsucrose (3) 11

    Figure S3.1. ¹H NMR (CDCl₃, 400 MHz) of 3 11

    Figure S3.2. ¹³C NMR (CDCl₃, 100 MHz) of 3 12

    Figure S3.3. DEPT of 3 13

    Figure S3.4. Elemental analysis of 3 14

Poly(1',2,3,3',4,4'-hexa-*O*-benzyl-6,6'-di-*O*-methacryloylsucrose)-co-polystyrene (4) 15

    Figure S4.1. IR (KBr) of 4 15

    Figure S4.2. ¹H NMR (CDCl₃, 400 MHz) of filtrate 4, [sug]/[st]= 0.056 16

    Figure S4.3. DSC of 4 17

    Figure S4.4. AFM of polymer 4, 7 μm, phase topography image, fast drying. 17

Poly(6,6'-di-*O*-allyl-1',2,3,3',4,4'-hexa-*O*-benzylsucrose)-co-polystyrene (5) 18

    Figure S5.1. IR (KBr) of 5 18

    Figure S5.2. ¹H NMR (CDCl₃, 400 MHz) of filtrate 5, [sug]/[st]=0.107 19

    Figure S5.3. DSC of 5 20

    Figure S5.4. AFM of polymer 5, 10 μm, height topography image, slow drying, lateral view. 20

References 21

1',2,3,3',4,4'-Hexa-*O*-benzylsucrose (1)

$[\alpha]_D^{20} +37.6$ (c 0.9, CHCl_3); Lit.¹ $[\alpha]_D +40.8$ (c 1.0, CHCl_3)

$R_f = 0.49$ (Hex-AcOEt, 1:2)

IR: ν_{max} (NaCl): 3380 (O-H), 3028 (C-H, stretch, unsaturated), 2916 (C-H, stretch, saturated), 1654, 1604 (Ar), 1496, 1453 (C-C, stretch), 1362 (C-H, assym.), 1065 (C-O-C, C-O-H, stretch), 732, 696 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.23 (m, 30H, Ar-H), 5.18 (s, 1H, H-1), 4.99-4.58 (m, 12H, H-4', H-6, H-5', Ar-CH₂), 4.22-4.14 (m, 1H, H-3'), 4.02-3.75 (m, 5H, H-3', 5, 6, 3), 3.75-3.62 (m, 3H, H-1', Ar-CH₂), 3.60-3.49 (m, 3H, Ar-CH₂), 3.45-3.28 (m, 3H, H-2, H-4, Ar-CH₂).

^{13}C NMR (100 MHz, CDCl_3) δ : 138.6, 138.3, 138.1, 138.0, 137.7 (C_q), 128.4, 127.9, 127.8, 127.7, 127.6 (C_{Ar}), 103.9 (C-2'), 90.7 (C-1), 83.5, 81.7, 81.0, 79.9, 79.5, 77.6 and 71.3 (C-2,3,3',4,4',5,5'), 75.6, 75.0, 73.4, 73.1, 73.0, 72.5 (C-1', 6 x OCH_2Ph), 61.9, 61.0 (C-6,6').

Figure S1.1. IR (NaCl) of 1

Figure S1.2. ^1H NMR (CDCl_3 , 400 MHz) of **1**

Figure S1.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **1**

1',2,3,3',4,4'-Hexa-*O*-benzyl-6,6'-di-*O*-methacryloylsucrose (**2**, new compound)

$[\alpha]_D^{20} +53.2$ (c 0.7, CHCl_3); no report in literature. IR: ν_{max} (NaCl): 3029 (C-H, stretch, insaturated), 2923 (C-H, stretch, saturated), 1720 (C=O), 1495, 1453 (C-C, stretch), 1295 (C-H, assym.), 1165 (C-C-O), 1089 (C-O-C, C-O-H, stretch), 1013, 944 (O-C-C, st as, ester, C-O-C, st sym, ether), 736, 697 (Ar) cm^{-1} .

^1H NMR (400 MHz, CDCl_3) δ : 7.39-7.21 (m, 35H, Ar-H), 6.09 (s, 1H, $=\text{CH}_2a$), 6.06 (s, 1H, $=\text{CH}_2a$), 5.74 (d, $J_{1,2} = 3.4$ Hz, 1H, H-1), 5.56 (s, 1H, $=\text{CH}_2b$), 5.46 (s, 1H, $=\text{CH}_2b$), 4.97 (d, $J = 10.6$ Hz, 1H, Ar- CH_2), 4.87 (d, $J = 10.8$ Hz, 1H, Ar- CH_2), 4.80 (d, $J = 10.6$ Hz, 1H, Ar- CH_2), 4.69-4.40 (m, 12H, Ar- CH_2 , H-3', 4', 6), 4.36-4.25 (m, 3H, H-1', 6'), 4.22-4.15 (m, 2H, H-1', 5), 4.14-4.07 (m, 1H, H-5'), 4.06-3.99 (m, 1H, H-3), 3.96 (d, $J = 9.2$ Hz, 1H, Ar- CH_2), 3.73 (d, $J = 10.8$ Hz, 1H, Ar- CH_2), 3.60-3.51 (m, 2H, Ar- CH_2 , H-4), 3.47 (dd, $J_{1,2} = 3.7$ Hz, $J_{2,3} = 9.6$ Hz, 1H, H-2), 1.94 (s, 3H, CH_3), 1.85 (s, 3H, CH_3).

^{13}C NMR (100 MHz, CDCl_3) δ : 167.0, 166.9 (COO-), 138.7, 138.2, 138.1, 137.9, 137.8, 137.7 (Cq benzyl groups), 136.2, 135.8, 128.4, 127.9, 127.9, 127.9 (Ar), 126.1, 125.5 ($=\text{CH}_2$), 104.5 (C-2'), 89.0 (C-1), 83.6, 81.9, 80.5, 79.7, 77.7, 77.2 and 69.2 (C-2,3,3',4,4',5,5'), 75.8, 74.9, 73.5, 73.3, 72.8, 71.9, 71.7 (C-1' + 6 OCH₂Ph), 64.2, 62.9 (C-6,6'), 18.4, 18.3 (CH_3).

MALDI TOF MS calcd $\text{C}_{62}\text{H}_{66}\text{O}_{13}\text{K}$: $[\text{M}]^+$ 1057.4140; found 1057.4150.

Figure S2.1. IR (NaCl) of 2

Figure S2.2. ^1H NMR (CDCl_3 , 400 MHz) of **2**

Figure S2.3. ^{13}C NMR (CDCl_3 , 100 MHz) of **2**

Figure S2.4. DEPT of 2

Figure S2.5. COSY of 2

Figure S2.6. HMQC of 2

Figure S2.7. MALDI-TOF of 2

6,6'- Di-*O*-allyl-1',2,3,3',4,4'-hexa-*O*-benzylsucrose (3)

$[\alpha]_D^{20} +30.2$ (c 1.2, CHCl_3); Lit.² $[\alpha]_D +29.9$ (c 1.0, CHCl_3).

$R_f = 0.47$ (Hex-AcOEt, 3:1)

^1H NMR (400 MHz, CDCl_3) δ : 7.40-7.19 (m, 30H, Ar-H), 5.92-5.80 (m, 2H, CH-allyl groups), 5.70 (d, $J_{1,2} = 3.5$ Hz, 1H, H-1), 5.24 (dd, $J_{HA,HB} = 17.2$ Hz, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 5.12 (dd, $J_{HA,HB} = 10.4$ Hz, 2H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 4.91 (d, $J = 10.9$ Hz, 1H, Ar- CH_2), 4.81 (d, $J = 10.9$ Hz, 1H, Ar- CH_2), 4.74 (d, $J = 10.9$ Hz, 1H, Ar- CH_2), 4.68-4.62 (m, Ar- CH_2 , 2H, H-6a), 4.58-4.35 (m, 11H, Ar- CH_2 , H-3', 4', 5 6b), 4.14 (t, $J_{3,4} = 7.2$ Hz, 1H, H-3), 4.11-4.04 (m, 2H, H-5', 6'a), 4.03-3.91 (m, 4H, $\text{OCH}_2\text{CH}=\text{CH}_2$), 3.74 (d, $J = 11.0$ Hz, 1H, Ar- CH_2), 3.71-3.50 (m, 6H, Ar- CH_2 , H-1', 4, 6'b), 3.40 (d, $J_{2,3} = 10.6$ Hz, 1H, H-2).

^{13}C NMR (100 MHz, CDCl_3) δ : 138.9, 138.7, 138.4, 138.3, 138.1, 138.0 (Cq benzyl groups), 134.7 (CH-allyl groups), 128.3, 128.3, 127.9, 127.7 (C_{Ar}), 116.9 ($\text{OCH}_2\text{CH}=\text{CH}_2$), 104.6 (C-2'), 90.1 (C-1), 84.0, 82.6, 82.0, 79.9, 79.7, 77.7 and 70.6 (C-2,3,3',4,4',5,5'), 75.5, 74.8, 73.4, 73.0, 72.5, 72.2, 71.5, 68.5 (C-1',6,6', $6\times\text{OCH}_2\text{Ph}$, $2\times\text{OCH}_2\text{CH}=\text{CH}_2$).

Anal. Calcd for $\text{C}_{60}\text{H}_{66}\text{O}_{11}$: C, 74.82; H, 6.91. Found: C, 74.96; H 7.19.

Figure S3.1. ^1H NMR (CDCl_3 , 400 MHz) of **3**

Figure S3.2. ¹³C NMR (CDCl₃, 100 MHz) of **3**

Figure S3.3. DEPT of 3

Figure S3.4. Elemental analysis of 3

Chemical Formula: C₆₀H₆₆O₁₁

Exact Mass: 962.4605

Molecular Weight: 963.1594

m/z: 962.46 (100.0%), 963.46 (65.3%), 964.47 (21.5%),
965.47 (6.1%), 964.46 (2.3%), 966.47 (1.2%)

Elemental Analysis: C, 74.82; H, 6.91; O, 18.27

Group No : 2	Element %			
Sample Name	Nitrogen%	Carbon%	Hydrogen%	Sulphur%
AA-006	0.00	74.88	7.22	0.00
AA-006	0.00	75.04	7.16	0.00

2 Sample(s) in Group No : 2				
Component Name	Average	Std. Dev.	% Rel. S. D.	Variance
Nitrogen%	0.00	0	0.0000	0.0000
Carbon%	74.96	.1131397	0.1509	0.0128
Hydrogen%	7.19	4.242637E-02	0.5901	0.0018
Sulphur%	0.00	0	0.0000	0.0000

Poly(1',2,3,3',4,4'-hexa-*O*-benzyl-6,6'-di-*O*-methacryloylsucrose)-co-polystyrene (4)

Figure S4.1. IR (KBr) of 4

Figure S4.2. ^1H NMR (CDCl_3 , 400 MHz) of filtrate 4, [sug]/[st]= 0.056

Figure S4.3. DSC of 4

Figure S4.4. AFM of polymer 4, 7 μm , phase topography image, fast drying.

Poly(6,6'-di-*O*-allyl-1',2,3,3',4,4'-hexa-*O*-benzylsucrose)-co-polystyrene (5)

Figure S5.1. IR (KBr) of 5

Figure S5.2. ^1H NMR (CDCl_3 , 400 MHz) of filtrate 5, $[\text{sug}]/[\text{st}]=0.107$

Figure S5.3. DSC of 5

Figure S5.4. AFM of polymer 5, 10 μm , height topography image, slow drying, lateral view.

References

1. M. Mach, S. Jarosz and A. Listkowski, *J. Carbohydr. Chem.*, **20**, 485-493 (2001).
2. B. Lewandowski, A. Listkowski, K. T. Petrova and S. Jarosz. in *Carbohydrate Chemistry: Proven Synthetic Methods*; P. Kovac, Ed.; CRC Press, Taylor & Francis Group, 2011, p 407-425.