Preparation and modification of PS-PMMA microspheres and their application in high performance liquid chromatography

Yu Wang^a, Jingyuan Xiao^a, Hongtao Cao^a, Jie Xing^a, Hailin Cong^{a,b}, Youqing

Shen^a, Bing Yu^{a,b*}

a. Institute of Biomedical Materials and Engineering, College of Materials Science

and Engineering, College of Chemistry and Chemical Engineering, Qingdao

University, Qingdao 266071, China

b. State Key Laboratory of Bio-Fibers and Eco-Textiles, Qingdao University,

Qingdao 266071, China

*Corresponding author: yubingqdu@yahoo.com

Postal address: Institute of Biomedical Materials and Engineering, Building D, Science Park,



Qingdao University, Qingdao 266071, China

Fig. S1 SEM image of PS seeds and particle size distribution.

Table. S1 The related parameters of different crosslinking degree.

Cross-linking	V _{MMA} (mL)	$V_{St}(mL)$	V _{DVB} (mL)	$M_{seed}\left(g ight)$
28%	0.50	1.45	0.65	0.26
38%	0.41	1.19	1.00	0.26
48%	0.35	1.02	1.24	0.26
68%	0.21	0.60	1.79	0.26
78%	0.13	0.38	2.09	0.26

1.The effects of different hydrolysis conditions on the properties of modified PS-PMMA

When ester groups on PS-PMMA are hydrolyzed, the different hydrolysis concentration and hydrolysis time will have certain effects on the properties of polymer porous microspheres. We first studied the hydrolysis of polymer microspheres in 2.5mol/L, 2mol/L, 1.5mol/L and 1.0mol/L NaOH solution respectively. The results are shown in Fig.S2, under the different hydrolysis concentrations, the hydrolyzed microspheres all show sphere fragmentation, and the degree of sphere fragmentation decreases with the decrease of alkaline hydrolysis concentration.



Fig .S2 Morphology of PS-PMMA with the same hydrolysis time (4 h) and different hydrolysis concentration :(a) 2.5 mol/L (b) 2 mol/L (c) 1.5 mol/L (d) 1.0 mol/L.

When the concentration of NaOH was adjusted to 0.7mol/L, it can be seen from Fig. S3 that the morphology of polymer microspheres changed with the continuous extension of hydrolysis time. The polymer microspheres not only collapsed, but also adhered to each other. With the prolongation of hydrolysis time, the adhesion became more and more serious.



Fig.S3 Morphology of PS-PMMA with different hydrolysis times at a hydrolysis concentration of 0.7mol/L :(a) 4 h (b) 6 h (c) 8 h (d) 10 h.

Compared with the hydrolysis concentration of 0.2 mol/L, when the concentration of NaOH was increased to 0.4 mol/L, the surface of the microspheres collapsed more seriously. With the prolongation of hydrolysis time, the surface of the microspheres showed different degrees of collapse deformation. This phenomenon will affect the mechanical properties of polymer microspheres. Fig. S4 (d) compared with Fig. S4 (a), it is obvious that the collapse marks on the surface of microspheres are deepened.



Fig. S4 Morphology of PS-PMMA with different hydrolysis times when the hydrolysis

concentration was 0.4 mol/L :(a) 4 h (b) 6 h (c) 8 h (d) 10 h.

2. Application part of HPLC

Table. S2 Gradient of mobile phase				
Time (min)	A (%)	B (%)		
0	99	1		
15	50	50		
30	0	100		

The specific separation conditions under the methanol/water mobile phase were 5 μ L of sample injection, 254 nm of UV detection wavelength, 23 °C of column temperature, and 0.6 mL/min of flow rate. As shown in Fig. S5, four chiral drugs (a) chlorpheniramine (b) benzoin (c) promethazine (d) D, L-amygdalic acid were separated

by chromatography using methanol/water (V:V=7:3) as the mobile phase. In the methanol/water mobile phase, only chlorpheniramine achieved complete separation, a certain degree of separation of promethazine was achieved, benzoin and D,L-amygdalic acid did not achieve the separation effect. In Fig.S5 (a) and Fig.S5 (c), the problem of peak stretching appeared in the chromatographic separation diagrams of chlorpheniramine and promethazine. The front and back edges of the peaks were not symmetrical, which might be caused by strong solvent polarity or overload of sample quantity. However, there is no peak stretching phenomenon in Fig.S5 (b) and Fig. S5 (d), but prominent peaks appear on the left and right sides of the peak respectively, which may be caused by poor sample separation effect due to inappropriate mobile phase system.



Fig. S5 Separation of chiral drugs by DR/vancomycin modified PS-PMMAP under

methanol/water mobile phase: Column specification: 75× 4.6mm; Temperature: 23 °C; Sample injection volume: 5 μL; Mobile phase: methanol/water (V: V = 7:3) mixed solution; UV detection wavelength: 254 nm; Samples: (a) chlorpheniramine (b) benzoin (c) promethazine (d) D, L-

amygdalic acid.