Supplementary material (ESI) for Journal of Materials Chemistry

Sugar-Modified Silanes: Precursors for Silica Monoliths

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Supplementary Material

Syntheses

CH_2=CH$CH_2(CH_2CH_2O)_nCH_2$CH=CH_2, ATPEO600: **ATPEO600**: To a solution of poly(ethylene glycol) (average MW 600, 6.0 g, *ca*.10 mmol) in THF (100 mL) at 0°C was added NaH (0.50 g, 20.8 mmol) slowly over 15 min. The mixture was allowed to warm up to room temperature and stirred for 5 h. The mixture was cooled down to 0 °C, allyl bromide (2.42 g, 20.0 mmol) was added. The mixture was warmed up to 40 °C and stirred for further 3 h. White precipitate was filtered off and washed with THF (3×10 mL). Combined filtrate and washing solution, THF was evaporated to give pale yellow crude product. The crude product was purified by chromatography (SiO_2, 10% ethyl acetate in hexane as eluent) give allyl terminated poly(ethylene glycol), **ATPEO600** as colorless oil, 6.1 g, (*ca.* 90% yield). ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 3.54-3.65 (m, 44H, PEO's OCH_2), 3.97 (dd, 2H, J=5.6Hz, J=1.1Hz CH_2=CHCH_2O), 3.98 (dd, 2H, J=5.6Hz, J=1.1Hz CH_2=CHCH_2O), 5.19 (m, 4H, CH_2=CHCH$_2$O), 5.88 (m, 2H, CH_2=CHCH$_2$O) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 69.4, 70.5 (PEO's OCH_2), 72.2 (CH_2=CHCH_2O), 117.1 (*C*H_2=CHCH$_2$O), 134.7 (CH_2=*C*HCH$_2$O) ppm. MS(maldi), *m/z*, 693 (5, M+Na^+, n=13), 671(4, M+1, n=13), 649 (8, M+Na^+, n=12), 627 (6, M+1, n=12), 605(12, M+Na^+, n=11), 583(6, M+1, n=11), 561(9, M+Na^+, n=10), 539 (5, M+1, n=10), 517(7, M+Na^+, n=9), 495(5, M+1, n=9), 473(6, M+Na^+, n=8), 42.1(100).

CH_2=CH$CH_2(CH_2CH_2O)_nCH_2$CH=CH_2, ATPEO2000: To a solution of poly(ethylene glycol) (average MW 2000, 2.0 g, *ca*.1 mmol) in THF (20 mL) at room temperature was added NaH (0.050 g, 2.1 mmol). The mixture was stirred at 50 °C for 2 h. Allyl bromide (0.24 g, 2.0 mmol) was added. The mixture was stirred at room temperature for further 10 h. White precipitate was filtered off and washed with THF (3×10 mL). Combined filtrate and washing solution, THF was evaporated to give pale brown crude product. The crude product was purified by chromatography (SiO_2, CH_2Cl_2 as eluent) give allyl terminated poly(ethylene glycol), **ATPEO2000** as white solid, 1.89 g, (*ca.* 91% yield). ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 3.50-3.65 (m, 180H, PEO's OCH_2), 3.97 (dd, 2H, J=5.6Hz, J=1.3Hz CH_2=CHCH_2O), 3.98 (dd, 2H, J=5.6Hz, J=1.3Hz CH_2=CHCH_2O), 5.16 (m, 4H, CH_2=CHCH$_2$O), 5.83 (m, 2H, CH_2=CHCH$_2$O) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 69.2, 70.3 (PEO's OCH_2), 72.2 (CH_2=CHCH_2O), 116.9 (*C*H_2=CHCH$_2$O), 134.5(CH_2=*C*HCH$_2$O) ppm.

CH_2=CH$CH_2(CH_2CH_2O)_nCH_2$CH=CH_2, ATPEO10K: To a solution of poly(ethylene glycol) (average MW 10K, 10 g, *ca*.1 mmol) in THF (100 mL) at room temperature was added NaH (0.050 g, 2.1 mmol). The mixture was stirred at 50 °C for 2 h. Allyl bromide (0.24 g, 2.0 mmol) was added. The mixture was stirred at room temperature for further 10 h. White precipitate was filtered off and washed with THF (3×20 mL). Combined filtrate and washing solution, THF was evaporated to give pale brown crude product. The crude product was dissolved in dichloromethane (20 mL), added to large amount of diethyl ether to give white precipitate. Repeated precipitate procedure once more gave allyl terminated poly(ethylene glycol), **ATPEO10K** as white solid, 7.9 g, (*ca.* 77% yield). ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 3.48-3.70 (m, 900H, PEO's OCH_2), 3.96 (m, 4H, CH_2=CHCH_2O), 5.18 (m, 4H, CH_2=CHCH$_2$O), 5.84 (m, 2H, CH_2=CHCH$_2$O) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 69.2-70.4 (PEO's OCH_2), 72.1 (CH_2=CHCH_2O), 116.9 (*C*H_2=CHCH$_2$O), 134.6(CH_2=*C*HCH$_2$O) ppm.

$(EtO)_3Si(CH_2)_3O(CH_2CH_2O)_n(CH_2)_3Si(EtO)_3$, TESiPEO600: To a mixture of ATPEO600 (2.1 g, *ca.* 3 mmol) and triethoxysilane (1.2 g, 6.9 mmol) one drop of Karsted's Pt catalyst was added. The mixture was stirred at room temperature for 1h (the reaction was monitored by ^{1}H NMR). The volatile organics was removed at 110°C under vacuum. The residue was diluted with CH_2Cl_2 (50 mL), activated charcoal (0.5 g) was added, the mixture was stirred at room temperature overnight. Filtered of charcoal, CH_2Cl_2 was evaporated off to give TESiPEO600 as colorless oil, 2.45g, *ca*. 80%yield. FTIR(neat), ν (cm^{-1}) 2975s, 2928s, 2884s, 2741w, 1741w, 1631w, 1459m, 1445m, 1391m, 1352w, 1297w, 1257w, 1107s, 1083s, 959m, 794m, 699w; ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 0.61 (m, 4H, SiCH_2), 1.20 (t, 18H, J=7.1 Hz, SiOCH$_2$CH_3), 1.64(m, 4H, SiCH$_2$CH_2CH$_2$), 3.41(m, 4H, SiCH$_2$CH$_2$CH_2), 3.57-3.63 (m, 56H, PEO's OCH_2), 3.80 (dd, 4H, J=7.1Hz, J=14.0Hz, SiOCH_2CH$_3$) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 6.5(Si*C*H$_2$), 18.4(SiOCH$_2$*C*H$_3$), 23.0(SiCH$_2$*C*H$_2$CH$_2$), 58.5(SiO*C*H$_2$CH$_3$), 70.1, 70.7 (PEO's O*C*H$_2$), 73.8 (SiCH$_2$CH$_2$*C*H$_2$) ppm.

$(EtO)_3Si(CH_2)_3O(CH_2CH_2O)_n(CH_2)_3Si(EtO)_3$, TESiPEO2000: To a mixture of ATPEO2000 (2.0g, *ca.* 1 mmol) and triethoxysilane (0.36g, 2.2 mmol) in dichloromethane (20 mL) one drop of Karsted's Pt catalyst was added. The mixture was stirred under refluxing for 3h (the reaction was monitored by ^{1}H NMR). The solvent was evaporated and thereafter the volatile organics was removed at 110 °C under vacuum. The residue was diluted with CH_2Cl_2 (50 mL), activated charcoal (0.5 g) was added, the mixture was stirred at room temperature overnight. Filtered of charcoal, CH_2Cl_2 solution was concentrated and thereafter added to large amount of diethyl ether to give TESiPEO2000 as colorless solid, 2.1g, *ca*. 88%yield. FTIR(neat, KBr), ν (cm^{-1}) 2975s, 2929s, 2885s, 1633w, 1459m, 1391s, 1366w, 1296w, 1262w, 1257w, 1194m, 1167s, 1106s, 1082s, 959s, 794s, 698w ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 0.89 (m, 4H, SiCH_2), 1.18 (t, 18H, J=7.1 Hz, SiOCH$_2$CH_3), 1.54(m, 4H, SiCH$_2$CH_2CH$_2$), 2.65(m, 4H, SiCH$_2$CH$_2$CH_2), 3.49-3.72 (m, 188H, PEO's OCH_2 and SiOCH_2CH$_3$, overlapped) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 10.4(Si*C*H$_2$), 18.1(SiOCH$_2$*C*H$_3$), 22.6(SiCH$_2$*C*H$_2$CH$_2$), 58.1(SiO*C*H$_2$CH$_3$), 69.2-70.2, overlapped (PEO's O*C*H$_2$ and SiCH$_2$CH$_2$*C*H$_2$) ppm.

$(EtO)_3Si(CH_2)_3O(CH_2CH_2O)_n(CH_2)_3Si(EtO)_3$, TESiPEO10K: To a mixture of ATPEO10K (5 g, *ca.* 0.5 mmol) and triethoxysilane (0.18 g, 1.1 mmol) in dichloromethane (50 mL) one drop of Karsted's Pt catalyst was added. The mixture was stirred refluxing for 5h (the reaction was

monitored by ^{1}H NMR). The solvent was evaporated and thereafter the volatile organics was removed at 110°C under vacuum. The residue was diluted with CH_2Cl_2 (100 mL), activated charcoal (1.0 g) was added, the mixture was stirred at room temperature overnight. Filtered of charcoal, CH_2Cl_2 solution was concentrated and thereafter added to large amount of diethyl ether to precipitate white solid. Repeated precipitation procedure gave TESiPEO10K as white solid, 2.7g, *ca*. 50% yield. FTIR(neat, KBr), ν (cm^{-1}) 2974s, 2929s, 2885s, 1631w, 1454m, 1391s, 1364w, 1266w, 1257w, 1167s, 1082s, 959m, 794m, 698w; ^{1}H NMR (200.2 MHz, $CDCl_3$): δ 0.66 (m, 4H, $SiCH_2$), 1.20 (m, 18H, $SiOCH_2CH_3$), 1.56(m, 4H, $SiCH_2CH_2CH_2$), 2.65(m, 4H, $SiCH_2CH_2CH_2$), 3.20-3.90 (m, 910H, PEO's OCH_2 and $SiOCH_2CH_3$, overlapped) ppm. ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 6.2($SiCH_2$), 18.0($SiOCH_2CH_3$), 23.0($SiCH_2CH_2CH_2$), 58.2($SiOCH_2CH_3$), 68.8-70.3, overlapped (PEO's OCH_2 and $SiCH_2CH_2CH_2$) ppm.

Figure S1: ^{29}Si NMR of DGS

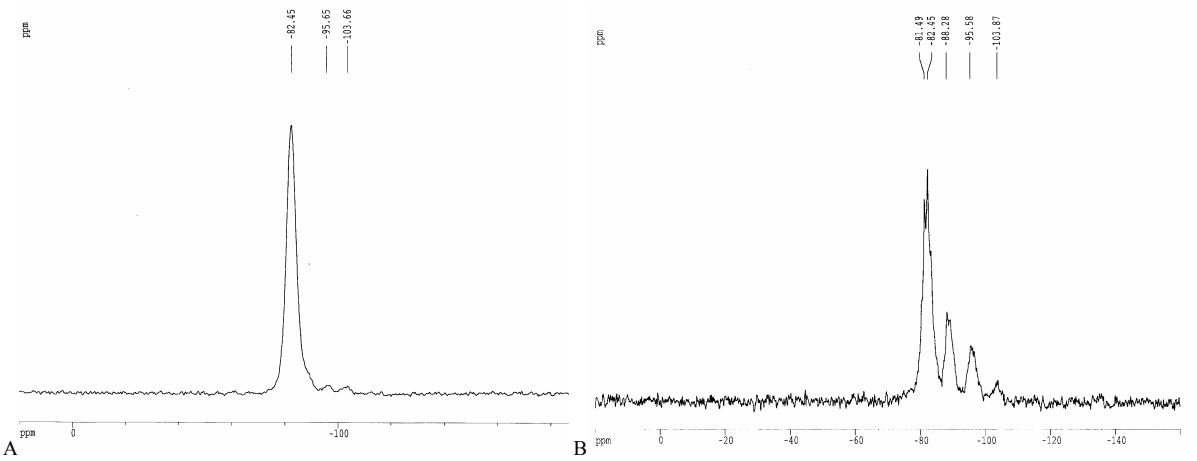

Figure S2: ^{29}Si NMR spectra of DGS prepared from A) dry glycerol distilled from Mg, freshly distilled TEOS, B) a "fresh" bottle of glycerol.

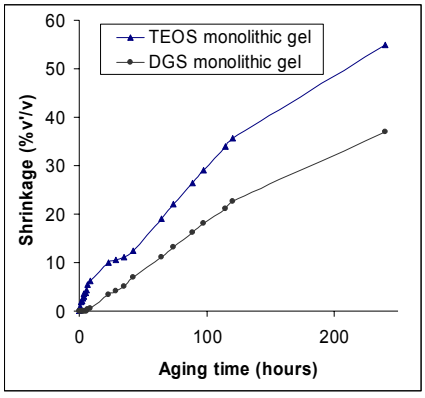

Figure S3: Comparison of rates of shrinkage for: A: TEOS (T-1) and DGS (D-1),over 10 days

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Table S1: Relationship between Glycerol Concentration and Gelation Time for **DGS** (Table 3A).

Entry	1	2	3	4	5
H_2O	300 µL	300 µL	300 µL	300 µL	300 µL
Glycerol	0 g	0.046 g	0.092 g	0.138 g	0.184 g
DGS	0.212 g	0.212 g	0.212 g	0.212 g	0.212 g
DGS:additional glycerol mole ratio	1:0	1:0.5	1:1	1:1.5	1:2
Added glycerol concentration	0 M	1.7 M	3.3 M	5 M	6.7 M
Total glycerol concentration	6.7 M	8.4 M	10.0 M	11.7 M	13.4 M
Gel time (min)	40	75	90	100	100

Table S2: Relation between Gel Time and Added Alcohols for TEOS-derived Silicas (Table 3B)

Net Molarity of alcohol OH groups	[EtOH] (mono-ol)	Gel time (h)	[$HOCH_2CH_2OH$] (di-ol)	Gel time (h)	[glycerol] (tri-ol)	Gel time (h)
0.63 M	0.63 M	12.5			0.21 M	13.5
0.84 M			0.42 M	13		
1.3 M	1.3 M	12			0.42 M	15
1.68 M			0.84 M	17		
1.9 M	1.9 M	11			0.63 M	19
2.5 M	2.5 M	9.5			0.84 M	19
2.6 M			1.3 M	17		
3.8 M	3.8 M	5			1.3 M	21.5
5.0 M	5.0 M	3.5	2.5 M	20.5	1.7 M	22.5
6.6 M			3.3 M	22.5		

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POROSITY

Table S3: Pore size and surface area data for monolithic silicas

Experiment Number		**T-1**	**D-1**	**D-2**
Precursor		TEOS	**DGS**	**DGS**/HSA
Surface Area Data (m^2/g)	Single point BET area	830	618	581
	Multi-point BET area	873	635	596
	Langmuir surface area	1721	1579	1668
	Micro pore area	781	527	473
	Meso pore area	91.8	108	124
	Cumulative adsorption surface area	494	534	593
	Cumulative desorption surface area	481	529	586
Pore Volume Data (cm^3/g)	Total pore volume	0.565 (< 50.0 nm)	0.467 (< 50.9 nm)	0.467 (< 56.2 nm)
	Cumulative adsorption pore volume(r=30-1 nm)	0.343	0.377	0.422
	Cumulative desorption pore volume (r=30-1 nm)	0.350	0.387	0.430
	Micro pore volume	0.449	0.357	0.342
Pore Size Data (nm)	Average pore radius	1.29	1.47	1.56

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Table S4: Pore size and surface area data for monolithic silicas with salt and protein dopants

Experiment Number		**D-1**	**D-6**	**D-2**	**D-7**
Additives		-	$MgCl_2$	HSA	$MgCl_2$/HSA
Surface Area Data (m^2/g)	Single point BET area	581	644	618	689
	Multi-point BET area	596	661	635	707
	Langmuir surface area	1668	3103	1579	2812
	Micro pore area	473	22.1	527	94.9
	Meso pore area	124	639	108	612
	Cumulative adsorption surface area	593	697	534	652
	Cumulative desorption surface area	586	794	529	754
Pore Volume Data (cm^3/g)	Total pore volume	0.467 (< 56.2 nm)	0.736 (< 53.9 nm)	0.467 (< 50.9 nm)	0.716 (< 45.6 nm)
	Cumulative adsorption pore volume(r=30-1 nm)	0.422	0.705	0.377	0.647
	Cumulative desorption pore volume (r=30-1 nm)	0.430	0.749	0.387	0.691
	Micro pore volume	0.342	0.0677	0.357	0.103
Pore Size Data (nm)	Average pore radius	1.56	2.27	1.47	2.03

Table S5: Pore size and surface area data for monolithic silicas with protein dopants

Experiment Number		**D-3**	**D-4**	**D-5**
HSA concentration (mM)		0	0.5	1
Surface Area Data (m^2/g)	Single point BET area	535	444	450
	Multi-point BET area	555	458	468
	Langmuir surface area	5732	4960	5142
Pore Volume Data (cm^3/g)	Total pore volume	0.965 (< 53.7 nm)	0.787 (<53.0nm)	0.838 (<53.9nm)
Pore Size Data (nm)	Average pore radius	3.48	3.43	3.58

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Table S4: Pore size and surface area data for monolithic silicas with PEO dopants

No		**D-1**	**D-8**	**D-9**
Precursor		**DGS**	PEO200	PEO10K
Surface Area Data (m^2/g)	Single point BET area	581	565	560
	Multi-point BET area	596	575	574
	Langmuir surface area	1668	1653	1915
	Micro pore area	473	418	268
	Meso pore area	124	157	305
	Cumulative adsorption surface area	593	503	548
	Cumulative desorption surface area	586	520	648
Pore Volume Data (cm^3/g)	Total pore volume	0.467 (< 56.2 nm)	0.476 (<51.2nm)	0.506 (<54.2nm)
	Cumulative adsorption pore volume(r=30-1 nm)	0.422	0.399	0.459
	Cumulative desorption pore volume (r=30-1 nm)	0.430	0.414	0.506
	Micro pore volume	0.342	0.306	0.210
Pore Size Data (nm)	Average pore radius	1.56	1.65	1.76

Table S5: Pore size and surface area data for monolithic silicas with silylated PEO dopants

No		**D-1**	**D-10**	**D-11**
Precursor		**DGS**	PEO(Si)200	PEO(Si)10K
Surface Area Data (m^2/g)	Single point BET area	581	323	374
	Multi-point BET area	596	331	390
	Langmuir surface area	1668	1215	2365
	Micro pore area	473	141	-
	Meso pore area	124	190	438
	Cumulative adsorption surface area	593	350	360
	Cumulative desorption surface area	586	387	409
Pore Volume Data (cm^3/g)	Total pore volume	0.467 (< 56.2 nm)	0.308 (<48.5nm)	0.596 (< 58.0 nm)
	Cumulative adsorption pore volume(r=30-1 nm)	0.422	0.295	0.557
	Cumulative desorption pore volume (r=30-1 nm)	0.430	0.313	0.579
	Micro pore volume	0.342	0.117	-
Pore Size Data (nm)	Average pore radius	1.56	1.87	3.06