Supporting Information

Amphiphilic Graft Copolymer Nanospheres: From Colloidal Self-assembly to CO\textsubscript{2} Capture Membranes

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FT-IR band assignment of PDMS-mMA, 4VP, and PDMS-g-P4VP(S)

FT-IR measurements were performed at a resolution of 4 cm\(^{-1}\) using a Spectrum 100 spectrometer (PerkinElmer).

**PDMS-mMA [IR, cm\(^{-1}\)]**: 2963 (w) \([\nu_a(C–H), CH_3]\), 1258 (m) \([\delta_s(CH_3), Si(CH_3)\_2]\), 950–1140 (m,s) \([\nu_a(Si–O), O–Si–O]\), 864 (vw) \([\rho(CH_3), Si(CH_3)\_2]\), 810 (w) \([\delta (Si–O), O–Si–O]\), 786 (s) \([\rho(CH_3), \nu (Si–C), Si(CH_3)\_2]\)

**4VP [IR, cm\(^{-1}\)]**: 1595 (s), 1547 (m), 1496 (w), 1408(s) \([in plane \nu(C–C, C–N), pyridine ring]\), 1219(w) \([in plane \delta(C–C, C–N), pyridine ring]\), 990 (m) \([ring breath]\), 924 (m) \([\omega(CH_2), aromatic vinyl compound]\), 829(s) \([out of plane \delta(C–C, C–N), pyridine ring]\), 786 (m), 453(m) \([\delta(C–C, C–N), pyridine ring]\)

**PDMS-g-P4VP(S) [IR, cm\(^{-1}\)]**: 3067 (w) \([\nu_{as}(CH_2), pyridine ring]\), 3024 (w)\([\nu_s(CH_2), pyridine ring]\), 2929 (w) \([\nu_{as}(CH_2), aliphatic chain]\), 2857 (w) \([\nu_s(CH_2), aliphatic chain]\), 1597 (s), 1557 (m), 1594 (w), 1416 (s) \([in plane \nu(C–C, C–N), pyridine ring]\), 1451(w) \([in plane \delta(CH_2), aliphatic chain]\), 1220(w) \([in plane \delta(C–C, C–N), pyridine ring]\), 1069 (m) \([skeletal \delta(C–C, C–N), pyridine ring]\), 970–1140 (sh) \([\nu_{as}(Si–O), O–Si–O]\), 864 (vw) \([\rho(CH_3), Si(CH_3)\_2]\), 994 (m) \([ring breath]\), 820 (s), 563 (s) \([out of plane \delta (C–C, C–N), pyridine ring]\), 798 (m) \([\rho(CH_3), \nu(Si–C), Si(CH_3)\_2]\)

Peak intensities are noted as strong (s), shoulder (sh), medium (m), weak (w), and very weak (vw). Vibrational modes are abbreviated as asymmetric stretching \((\nu_a)\), symmetric stretching \((\nu_s)\), deformation \((\delta)\), wagging \((\omega)\), rocking \((\rho)\), and twisting \((\tau)\).
1H-NMR band assignment of PDMS-g-P4VP

Synthesized polymer colloids in deuterated chloroform (CDCl3) at a concentration of 2 wt% were analyzed by 1H-NMR using a 600MHz high-resolution spectrometer (Avance 600, Bruker, Germany) using tetramethylsilane ((CH3)4Si) as an internal standard set at 0 ppm.

1H-NMR (CDCl3, 600 MHz): δ 0.05–0.08 [s, Si(CH3)2, Hj] 0.55 [s, CH2, Hi], 0.87 [m, CH3, Hl, Hf], 1.4 [m, CH2, Hc, Hh, Hk], 1.90 [s, CH2, Hg], 1.80 [s, CH2, He] 2.1 [m, CH, Hd], 3.36–3.40 [m, CH2, Hg], 6.21–6.67 [m, C–H, Hb in pyridine], 7.27 (CDCl3), 8.15–8.47 [m, C–H, Ha in pyridine]. Hydrogens were tagged Hi (i = a,b,c,...) in Figure 1c.

The molecular weight of PDMS-g-P4VP graft copolymer was determined by gel permeation chromatography (Ultimate 3000 Thermo, USA) equipped with a column (solux KD 806) and a refractive index detector (RI 520 RefractoMax), using dimethylformamide as an eluent, calibrated by poly(methyl methacrylate) standards. Colloid nanostructures were investigated by energy filtered TEM using a LIBRA 120 instrument (Carl Zeiss, Germany) operating at an accelerating electron beam voltage of 120 kV. One or two drops of approximately 1 wt% polymer in cyclohexane were cast onto a carbon coated TEM grid and dried at room temperature overnight to prepare the samples. Specimens for ultrathin cross-sectional TEM imaging were obtained by fixing the colloids at the end of small tips filled with commercial epoxy resin (Spuur low-viscosity embedding kit) without air bubble formation. Initial viscous epoxy resin/crosslinking agent liquid mixtures were oven-cured at 70 °C for over 12 h. The solidified colloid-containing resin was cut into of approximately 200 nm-thick slices using an ultra-microtome (EM UC7, Leica, Germany). Individual ultra-thin sections were floated on water, loaded on the TEM grid, and stored in the presence of a desiccant before TEM...
measurement. The colloid surface was coated with a 10 nm-thick Pt layer by sputtering (BAL-TEC/SCD 005) at a current of 30 mA for 120 s before SEM observation (SUPRA 55VP, Carl Zeiss, Germany). The average membrane thickness was considered to determine permeability. Each PSf-supported membrane was cryogenically fractured in liquid nitrogen and coated with a 10 nm Pt film before SEM thickness measurements were conducted at ten different points. Particle sizes and size distributions of PDMS-g-P4VP(S) dispersions in cyclohexane were measured by DLS (Zetasizernano zs90 system, Malvern). CO2 uptake was measured at 298K by volumetric gas adsorption technique with BELSORP-mini II (BEL JAPAN, INC). Energy-dispersive X-ray spectroscopy was performed using an XFLASH detector 4070 (Bruker).
**Figure S1.** FE-SEM images of (a,b) PDMS-g-P4VP(S), (c,d) PDMS-g-P4VP(L), and (e,f) P4VP.
**Figure S2.** FE-SEM images of PDMS-g-P4VP(S) colloids (a,b) in long-range hexagonally close-packed arrays at low magnification and (c,d) in cubic arrays at high magnification.
**Figure S3.** Photographs of PDMS-g-P4VP(S) nanospheres dispersions after (a) 0 min, (b) 1 hr, (c) 12hr, (d) 21hr in different solvents such as normal hexane, cyclohexane, toluene, ethyl acetate and tetrahydrofuran.
Figure S4. TEM images of (a,b) PDMS-g-P4VP(S), (c) PDMS-g-P4VP(L), and (d) PDMS-g-P4VP(S) cross-sections.
**Figure S5.** SEM-EDS analysis of (a, b) PDMS-g-P4VP(S) and (c, d) PDMS-g-P4VP(L) nanospheres.
Figure S6. DLS of PDMS-g-P4VP(S) colloids in cyclohexane.
Table S1. Solubility and Flory–Huggins interaction parameters of solvents and polymers.

<table>
<thead>
<tr>
<th></th>
<th>Hildebrand $\delta$ (MPa)$^{0.5}$</th>
<th>Molar Volume (cm$^3$/mole)</th>
<th>Hansen $\delta_D$ (MPa)$^{0.5}$</th>
<th>Hansen $\delta_p$ (MPa)$^{0.5}$</th>
<th>Hansen $\delta_H$ (MPa)$^{0.5}$</th>
<th>Relative evaporation rate</th>
<th>$\chi_{\text{solvent-PDMS}}$</th>
<th>$\chi_{\text{solvent-P4VP}}$</th>
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</thead>
<tbody>
<tr>
<td>n-Hexane</td>
<td>14.7</td>
<td>131.6</td>
<td>14.9</td>
<td>0</td>
<td>0</td>
<td>9</td>
<td>0.34</td>
<td>2.48</td>
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<tr>
<td>Cyclohexane</td>
<td>16.8</td>
<td>108.7</td>
<td>16.8</td>
<td>0</td>
<td>0.2</td>
<td>7</td>
<td>0.45</td>
<td>1.45</td>
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<tr>
<td>Toluene</td>
<td>18.2</td>
<td>106.8</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
<td>2</td>
<td>0.68</td>
<td>0.95</td>
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<tr>
<td>Ethyl acetate</td>
<td>18.6</td>
<td>98.5</td>
<td>15.8</td>
<td>5.3</td>
<td>7.2</td>
<td>4</td>
<td>0.76</td>
<td>0.83</td>
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<tr>
<td>THF</td>
<td>19.4</td>
<td>81.7</td>
<td>16.8</td>
<td>5.7</td>
<td>8.0</td>
<td>6</td>
<td>0.96</td>
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* Flory–Huggins interaction parameters ($\chi_{s-p}$) between a solvent and a polymer were calculated using the empirical equation for a nonpolar system, $\chi_{s-p} = 0.34 + \frac{V_s(\delta_s - \delta_p)^2}{RT}$, where $V_s$ is the molar volume of the solvent while $\delta_s$ and $\delta_p$ are the Hildebrand solubility parameters for solvent and polymer, respectively. A solvent–polymer pair is completely soluble when the Flory–Huggins interaction parameter is less than 0.5.