Nanostructured Membranes from Soft and Hard Nanoparticles Prepared via RAFT-mediated PISA

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Abstract

RAFT dispersion polymerization of benzyl methacrylate (BzMA) was used to prepare a series of near mono-dispersed poly(2-(dimethylamino)ethyl methacrylate)-poly(benzyl methacrylate) (PDMA-PBzMA) diblock copolymer nanoparticles in a ethanol/ water binary mixture via polymerization-induced self-assembly (PISA). A relatively long $PDMA_{88}$ chain transfer agent was targeted to ensure that only spherical morphologies were obtained. High (>99 %) BzMA monomer conversions could be achieved within 24 h when targeting degrees of polymerisation (DP) of up to 1000. The resulting particles were analyzed using DLS and TEM. Particles with PBzMA DPs of 500 and 1000 were used as templates for deposition of silica particles. TEM images confirmed that TMOS precursor was successfully converted into silica sols that were deposited on the surface of the spherical polymer nanoparticles. Thin film membranes were then prepared from these silicified spherical particles (hard spheres) as well as the initial spherical particles devoid of silica coating (soft spheres). These membranes were fully characterized using SEM, AFM and water filtration test.
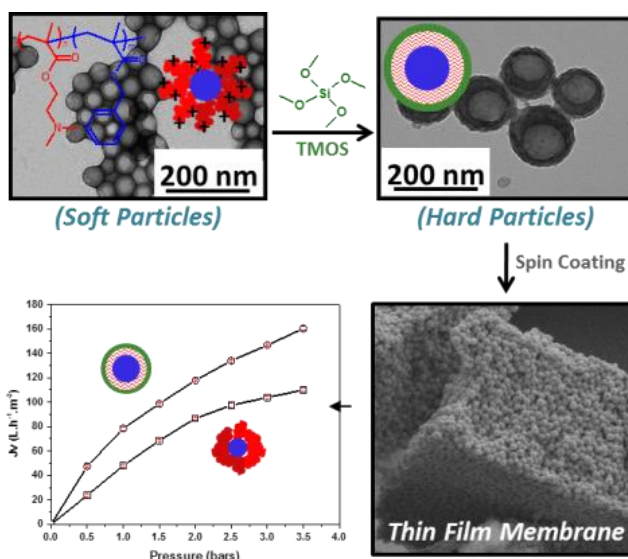
Introduction

Membranes are an essential part of the majority of industrial processes from pharmaceutics and food production, to water filtration/recycling and chemical industry.[1-3] An efficient membrane would need to have regular pores with sharp molecular cut off, and should be robust and mechanically stable. Block copolymers are great candidates for making selective membranes with regular pore size and good mechanical stability since they are highly processable. Polymeric membranes have been made from block copolymers using different techniques such as spin-coating, extrusion, and bulk evaporation.[4] The main disadvantage of these methods is the need for post-fabrication modifications to introduce porosity into the films. This extra step is often not favoured industrially since it increases the production cost. Recently the use of block copolymer particles in the fabrication of porous membranes has been demonstrated.[5-10] Membranes prepared from spherical polymer particles can have relatively well-controlled pore size since the particle diameter dictates the surface area of the gap present in the hexagonally packed spherical particles assembly forming the membrane pores. One of the main drawbacks of membranes made from colloidal polymer particles is their relative fragility especially when dry (they tend to crack and peal when completely dry) or under high pressure (high pressures often compress and deform soft polymer particles). Polymerization induced self-assembly is a unique method that allows the facile synthesis of polymer nanoparticles without need for any post polymerization step. Also this technique allows the fabrication of nanoparticles at high concentration which is beneficial for the fabrication of membranes from colloidal particles. In the past few years, there have been many reports on RAFT dispersion polymerization formulations using functional macro-CTAs in different media (water, alcohol, alkane).[11-13] RAFT dispersion polymerization protocol based on the chain extension of a poly(2-(dimethylamino)ethyl methacrylate) (PDMA) macro-CTA using benzyl methacrylate (BzMA) in ethanol or ethanol/water mixtures have

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been reported previously.[14-15] It was demonstrated that using a 80/20 ethanol-water binary mixture allows reaching high monomer conversion and high DPs of PBzMA within 24h with good control over the molar mass and the dispersity of the diblock copolymer chains. It was shown that the use of a long PDMA macro-CTA limits the morphology of the resulting particles to kinetically-trapped spheres, allowing targeting higher DPs for the core-forming block. The choice of PDMA stabilizing group also allows the introduction of positive charge on the surface of the particles. This positive charge could be used to deposit silica particles (synthesized via an *in-situ* sol-gel reaction) on the surface of the PDMA-stabilized particles.[16] Such core-shell spherical particles would benefit from the properties of both the soft polymer and the rigid silica particles. Making membranes from colloidal silica coated particles could allow easy preparation of isoporous membranes endowed with higher resistance to dryness, high pressure and aggressive chemicals such as chlorine (often used to clean membranes).

In the present article, a relatively long PDMA macro-CTA (DP= 88) was used to produce a series of PDMA-PBzMA block copolymer spherical particles via polymerization induced self-assembly in an 80/20 ethanol/water binary mixture at 70°C. The long macro-CTA allowed varying the DP of the core forming PBzMA block up to 1000 reaching full conversion of the BzMA. Selected PDMA-PBzMA particles (according to their sizes) were coated with silica sols via a sol-gel reaction using TMOS. Thin film membranes were then prepared from the silica-coated particles and their porosity, permeation and performance were assessed against membranes prepared from uncoated (naked) counterparts. All the particles and membranes prepared were fully characterized using different microscopy methods such as AFM, SEM and TEM.

Experimental

Materials. All reagents were purchased from Sigma-Aldrich France and used as received unless otherwise noted. Either 4,4'-Azobis(4-cyanovaleric acid) (ACVA) or 2,2'-

azobisisobutyronitrile (AIBN) was used as an initiator. Benzyl methacrylate was passed through an inhibitor removal column (also purchased from Sigma) prior to use. 4-Cyano-4-(2-phenylethanesulfanylthiocarbonyl) sulfanylpentanoic acid (PETTC) was synthesized as reported previously.[17] $CDCl_3$ and CD_2Cl_2 were purchased from Eurisotop, Saint Aubin, France.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate) (PDMA) macro-CTA. A round-bottomed flask was charged with 2-(dimethylamino) ethyl methacrylate (DMA; 10.0 g, 63.6 mmol), PETTC (191 mg, 0.6 mmol), ACVA (32 mg, 0.1 mmol) and THF (10.0 g) (target DP = 90). The sealed reaction vessel was purged with nitrogen and placed in a pre-heated oil bath at 70˚C for 8 h. The resulting polymer (monomer conversion = 87 %; Mn = 14,800 g mol^{-1}, Mw/Mn = 1.09) was purified by precipitation into excess hexane. The mean degree of polymerisation (DP) of this PDMA macro-CTA was calculated to be 88 using ^{1}H NMR spectroscopy (in $CDCl_3$ or CD_2Cl_2) by comparing the integrated signals corresponding to the aromatic protons at 7.2 - 7.4 ppm with those due to the methacrylic polymer backbone at 0.4 - 2.5 ppm.

Synthesis of poly(2-(dimethylamino)ethyl methacrylate)-poly(benzyl methacrylate) (PDMA-PBzMA) diblock copolymer particles via dispersion polymerisation in ethanol/H_2O mixture.

In a typical RAFT dispersion polymerisation synthesis conducted at 20 % w/w total solids, BzMA (1.00 g, 8.7 mmol), AIBN (0.90 mg, 0.006 mmol), PDMA$_{88}$ macro- CTA (392.6 mg, 0.028 mmol) was dissolved in 5.6 g of ethanol/water mixture (80/20). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen gas for 10 minutes and then placed in a pre-heated oil bath at 70˚C for 24 h. The final monomer conversion was determined by ^{1}H NMR analysis in $CDCl_3$ or CD_2Cl_2 by integrating the PBzMA peak (CH_2) at 4.9 ppm to BzMA monomer vinyl peaks (CH_2) at 5.2 and 5.4 ppm.

In further PDMA-PBzMA diblock copolymer syntheses, the mean DP of the PBzMA block was systematically varied (12, 220, 500 and 1000) by adjusting the amount of BzMA monomer.

Silicification of PDMA-PBzMA diblock copolymer nanoparticles. In a typical silicification reaction, 3.0 g of a 20 % w/w dispersion of PDMA-PBzMA diblock copolymer nanoparticles in ethanol was diluted with ethanol (0.524 g) and water (2.567 g). The pH of the resulting 10% w/w dispersion was adjusted to pH 4 using 50 % acetic acid. Tetramethyl orthosilicate (TMOS) was then added (diblock: TMOS mass ratio = 1:1.1) and the reaction solution was stirred at 25˚C overnight. This dispersion was then diluted with ethanol (19 g) to 5 % w/w total solids and pH was adjusted to 2 by addition of concentrated HNO_3. The ratio of diblock: TMOS was varied to 1/1.25 and 1/5 to target different silica shell thicknesses.

Analysis and characterization of block copolymers

Copolymer molar mass distributions were determined using size exclusion chromatography (SEC) performed with a double detector array from Viscotek (TDA 305, Malvern instruments, Worcestershire, UK). The Viscotek SEC apparatus was equipped with two mixed-columns with common particle size of 5 μm using THF as an eluent (1.0 ml/min). The Viscotek system contains a refractive index detector (RI, concentration detector), and a four-capillary differential viscometer. OmniSEC software was used for data analysis and acquisition. The number average molar mass (*Mn*) and dispersity index (*Mw/Mn or Ð*) were calculated relative to polystyrene standards.

^{1}H NMR spectra were acquired with Bruker 300 Mhz spectrometer using $CDCl_3$ solvent.

Dynamic light scattering (DLS) measurements were conducted using a Malvern Instruments Zetasizer Nano series instrument equipped with a 4 mW He-Ne laser operating at 633 nm, an avalanche photodiode detector with high quantum efficiency, and an ALV/LSE-5003 multiple tau digital correlator electronics system.

Transmission electron microscopy (TEM) studies were conducted using a JEOL 1200 EXII instrument operating at 120 kV equipped with a numerical camera. To prepare TEM samples, 5.0 µL of a dilute copolymer solution was placed onto a carbon-coated copper grid, stained (only polymeric samples) using an aqueous solution of Ammonium molybdate 99.98%, and then dried under ambient conditions.

Thermogravimetric analysis (TGA) was conducted on vacuum-dried samples using a TA Instruments Q500 thermogravimetric analyser. Samples were heated from 25°C to 800 °C in N_2 at a heating rate of 10°C min^{-1}. This protocol ensured complete pyrolysis of the organic component. The results were treated using Universal Analysis software.

Filtration and membrane characterizations

Thin film membranes were prepared via deposition of the colloidal dispersion of the nanoparticles on a commercial Nylon membrane (average pore size of 0.2 µm) using a SPS Spin 150 spin coater at 1000 rpm for 120 sec with a speed of 100 rpm.s^{-1} under dry argon atmosphere. Four different membranes were prepared from bare and silica coated particles of $PDMA_{88}$-$PBzMA_{500}$ and $PDMA_{88}$-$PBzMA_{1000}$.

SEM analysis was conducted using a Hitachi S-4500 instrument operating at a spatial resolution of 1.5 nm at 15 kV energy. The samples were dried and coated with an ultrathin layer of electrically conducting platinum deposited by high vacuum evaporation.

AFM images were obtained with a Pico SPM II provided by Molecular Imaging. The imagery was controlled by the PicoView 1.10 software. The experiments were all carried out in tapping mode. The types of tips used were PPS-FMR purchased from Nanosensors with a frequency resonance between 45-115 kHz and a force constant between 0.5-9.5 N/m. Gwyddion 2.25 software was used to treat the images.

For filtration tests the prepared membrane (d=2.5 cm) was fitted in a 10 mL filtration cell (Amicon 8010 stirred cell). Then filtration cell was connected to a water reservoir and

compressed air line. The measurements were then performed at pressures between 0.1 and 4.0 bars. The mass of the water passing through the membrane (permeate) is recorded by the SartoConnect software at regular time intervals. All filtration experiments were performed at room temperature with dust free ultrapure water (filtered through a 400 micron filter).

Results and Discussion

A PDMA macro-CTA was synthesised by RAFT solution polymerisation in THF (Scheme 1) following a method reported previously.[18] However, in this work a higher DP (up to DP= 1000) was targeted to ensure the exclusive formation of spherical particles. After purification, the DP of this PDMA macro-CTA was calculated to be 88 by ^{1}H NMR. This PDMA$_{88}$ macro-CTA was then chain-extended with PBzMA via RAFT dispersion polymerisation, in an ethanol/water binary mixture, at 70°C, to produce a series of PDMA$_{88}$-PBzMA$_x$ diblock copolymer nanoparticles. Reactions were conducted at a total solids content of 20 % w/w with the target DP, x, for PBzMA varied between 120 and 1000 (Figure S1). Each polymerisation was carried out for 24 h and then analysed by ^{1}H NMR, THF SEC, DLS and TEM; the results are summarised in Table S1. As described in a previous publication the dispersion polymerization of BzMA was conducted in a mixture of ethanol/water to reach high monomer conversion in a short time.[15] This rate enhancement is due to stronger partitioning of the BzMA monomer, which is soluble in ethanol but insoluble in water. This means that, following the onset of micellisation, unreacted BzMA preferentially enters the micelles, increasing the local monomer concentration and thus increasing the rate of BzMA polymerization. Addition of water is also beneficial in this work since it results in the protonation of some of the PDMA chains (acquiring positive charge).[19,20] As reported previously these positive charges force the growing PDMA-PBzMA chains to self-assemble into spherical particles rather than higher order morphologies.[20] As expected and shown in

Figure S1, the five different PBzMA block length led to the formation of spherical particles, the size of which increases linearly (average hydrodynamic diameter from 65 nm to 260 nm) with the DP of the core forming PBzMA block. As seen in Figure S1(f), the obtained hydrodynamic diameter is slightly bigger than the average diameters calculated from TEM images. This slight difference arises from the fact that the stabilizing chains are collapsed on the surface of the particles at dry state and does not contribute to the calculated particle size.
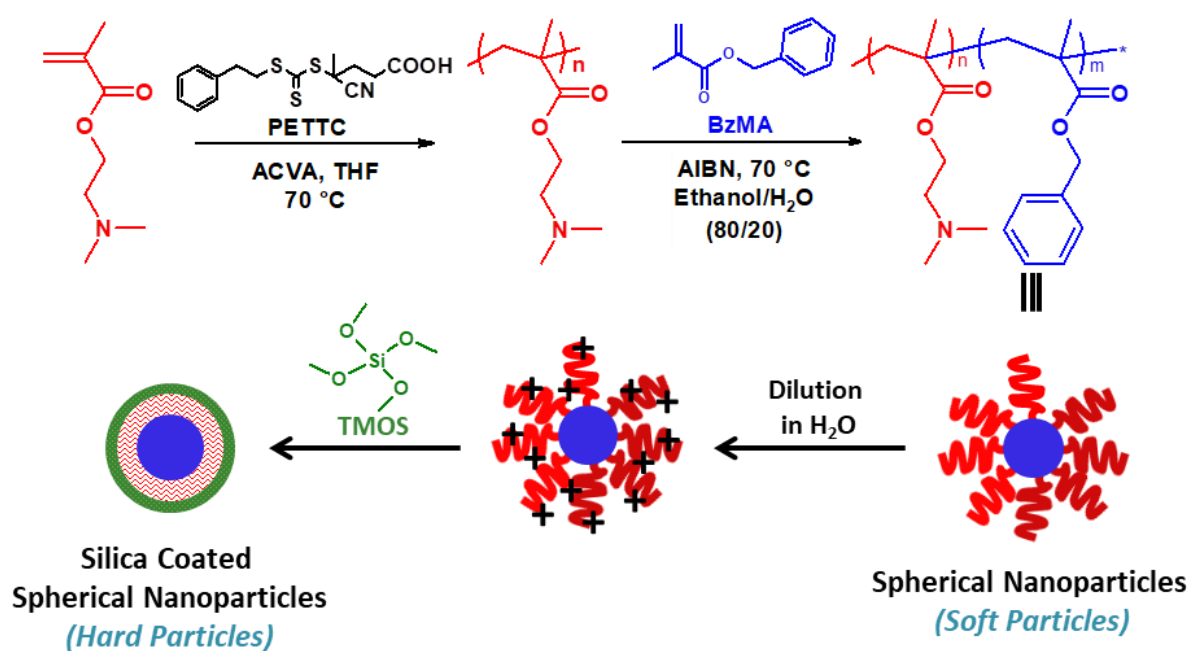
Scheme 1. Synthesis of a poly(2-dimethylamino)ethyl methacrylate (PDMA) macro-CTA by RAFT solution polymerisation, using PETTC as CTA, and subsequent chain extension with benzyl methacrylate (BzMA) by RAFT dispersion polymerisation to produce sterically stabilised PDMA-PBzMA diblock copolymer nanoparticles; and silica deposition through sol-gel reaction.

The rest of the study was performed using the two batches of largest particles (PBzMA DPs of 500 and 1000) because it is easier to obtain clear images with bigger particles. Thin film membranes deposited onto a commercially available Nylon support were prepared from these spherical particles using spin-coating. Figure 1 show the surface and the cross section of the prepared membranes obtained using AFM and SEM. As it can be seen monodisperse

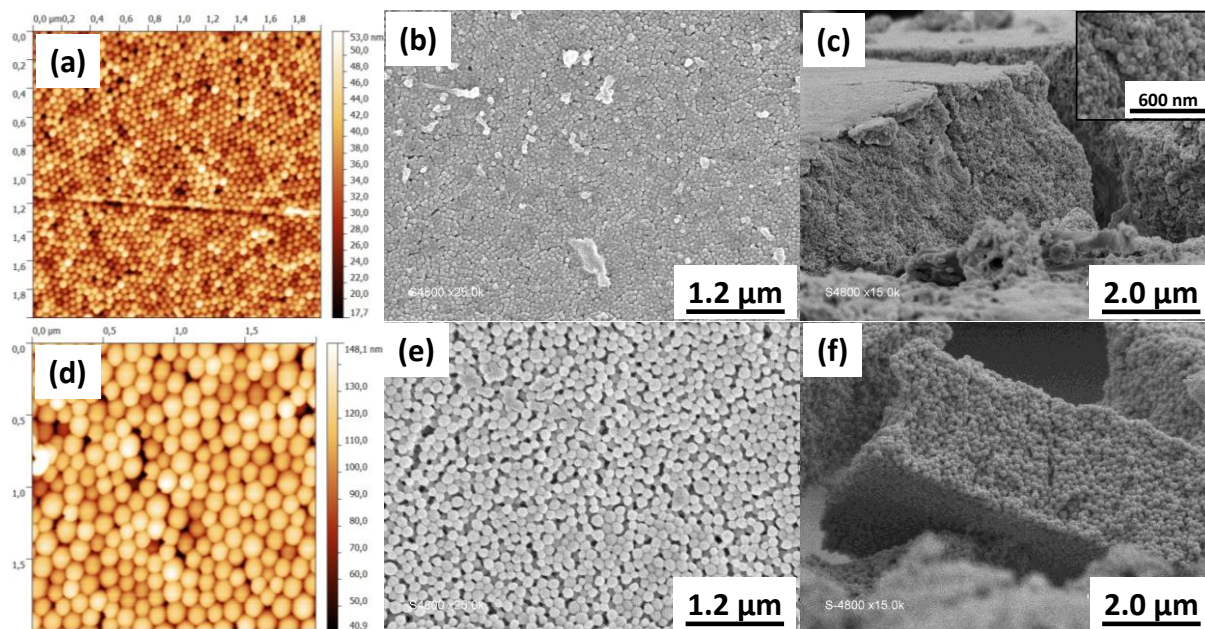spherical particles form a homogeneous thin layer in a compact hexagonally packed arrangement.

Figure 1. AFM and SEM images of films prepared from PDMA$_{88}$-PBzMA$_x$ diblock copolymer spheres (a, b) film top surface x= 500 (c) film cross section x= 500 (d, e) film top surface x= 1000 (f) film cross section x= 1000.

The two batches of PDMA$_{88}$-PBzMA$_x$ spherical particles (x= 500 and 1000) were then silicified using an acid catalysed protocol. Particles were diluted down to 10 % w/w solids in a 2:1 ethanol/water binary mixture. The pH of the solution was adjusted to 4 using acetic acid. TMOS was then added and the reaction mixture was stirred at 25˚C overnight (17 h). TEM studies (Figure 2) confirmed that small silica particles were deposited on the surface of the PDMA-PBzMA particles. It is important to note that the TEM images of these particles were obtained without using any stain. This is an additional proof that the silica is present on the surface of the particles as it is the high electron contrast conferred by the silica that makes the imaging possible.

Our attempts to measure and calculate the silica shell thickness was unsuccessful. Calculations based on the diameter of the template (spherical particles) and the amount of

TMOS added did not lead to a meaningful trend as not all the produced silica was deposited on the spherical particles. The shell thickness measured from the TEM images (measurements done on 100 particles using ImageJ software) suggest that the shell thickness increased from 2 to 9 nm for smaller particles (DP $_{PBzMA}$ = 500) and from 2 to 11 nm for the bigger particles (DP $_{PBzMA}$ = 1000) when the TMOS/copolymer ratio was increased from 1.1 to 5 (Table S2). TGA analysis was also used to get the silica content of the coated particles. The obtained silica mass % from TGA analysis indicates that the amount silica deposited on the surface of the particles increased as the TMOS/copolymer mass ratio was increased (for both particle sizes, see Table S2). The accuracy of these values is very low because: (1) all of the added TMOS may not have reacted (2) all the silica sols generated may not have deposited on the particles (secondary nucleation). Hence these values should be considered only as an approximation.
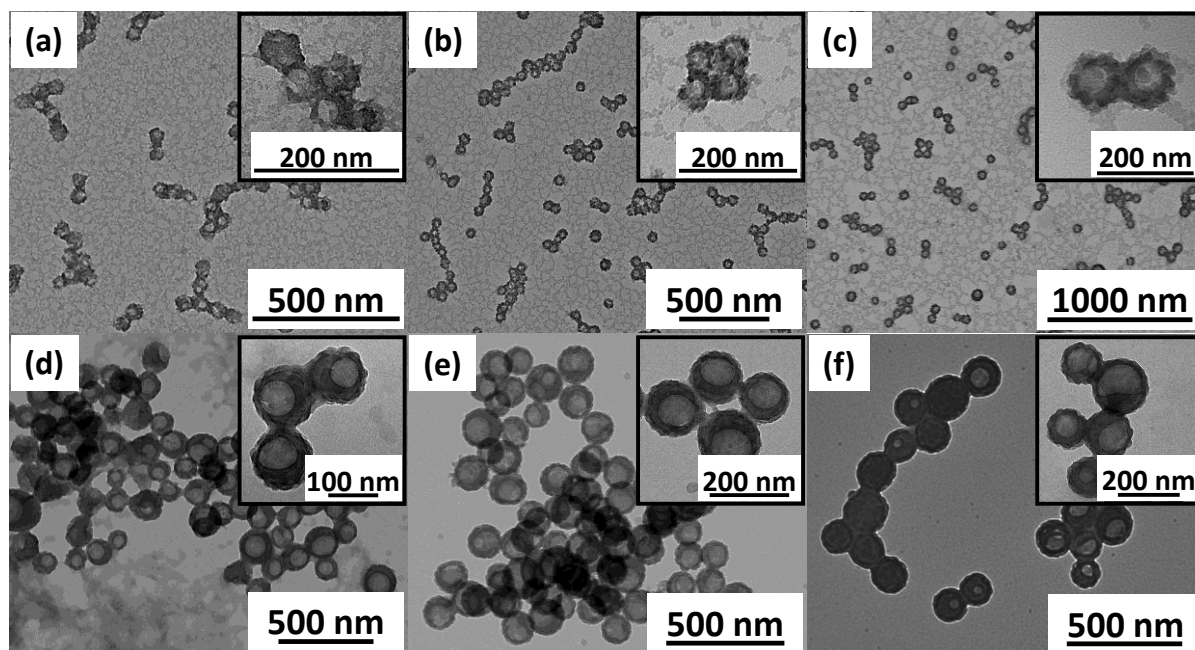

Figure 2. TEM images of silica coated PDMA$_{88}$-PBzMA$_{x}$ spherical particles prepared using different ratios of TMOS to Diblock copolymer (a) x= 500, 1.1: 1 (b) x= 500, 2.5: 1 (c) x= 500, 5: 1 (d) x= 1000, 1.1: 1 (b) x= 100, 2.5: 1 (c) x= 100, 5: 1.

Four thin film membranes prepared from colloidal solution containing $PDMA_{88}$-$PBzMA_{500}$ and $PDMA_{88}$-$PBzMA_{1000}$ particles (Figure 1) and their silicified counterparts were prepared on a nylon support (average pore size of 0.2 μm) using spin-coating under inert atmosphere. Membranes prepared from naked (non-silicified) samples had to be dried slowly under controlled atmosphere and kept moist to avoid fissures. In contrast, membranes prepared from silicified particles could be dried at ambient temperature and atmosphere and could be stored in dry state. SEM images (Figure 3) of the top surface of the membranes prepared from silicified particles show a homogeneous layer. The cross sections of these membranes (Figure 3b and 3d) display a compact arrangement of the silica coated spherical particles throughout the thickness of the membranes. A closer look at the SEM images of the coated particles (inset Figure 3a and 3c) at a higher magnification, reveals a coarse surface (almost raspberry like). This roughness could hinder the formation of regular pores in the membrane. The AFM images of the top surface of the membranes also confirmed the compact assembly of the particles into a thin film (Figure S5). The porosity of the membranes was tested via filtration of pure water using a dead-end filtration cell (Millipore -10 mL). The dead-end filtration cell was filled with water at pH 7.1 and connected to a pressurized water reservoir. To ensure the stability of the membranes, they were kept at each pressure for 30 minutes prior to data collection. The setup pressure was increased gradually from 0 to 3.5 bars. The flux values were calculated based on Darcy's law (Eq. S1) using data obtained for 3 full cycles (increasing from 0 to 3.5 bar and then decreasing to 0 bar). Figure 4a shows the evolution of flux (J_v) for membranes prepared from naked and silicified $PDMA_{88}$-$PBzMA_{500}$ spherical particles. The membranes prepared from naked spheres had a flux value of 40 $L.h^{-1}.m^{-2}$ at 3.5 bars. At the same pressure the flux value was almost double (80 $L.h^{-1}.m^{-2}$) when the equivalent silicified particles were used. The membranes prepared from bigger particles ($PDMA_{88}$-$PBzMA_{1000}$) followed a similar trend. The uncoated particles had a flux value of

about 100 L.h^{-1}.m^{-2} at 3.5 bar while membranes prepared from silica-coated particles had a flux of 160 L.h^{-1}.m^{-2} (Figure 4b). ==Membranes prepared from bigger spherical particles (PDMA$_{88}$-PBzMA$_{1000}$) were unsurprisingly more permeable than the membranes with smaller particles (PDMA$_{88}$-PBzMA$_{500}$) since their pore size is smaller (compact packing of bigger spheres will lead to larger pores).== Silica-coated particles possessed a rougher surface (raspberry like morphology) due to the deposition of very small silica sols. This roughness could lead to bigger pore sizes when forming the thin layer membrane since the particles with rough surface may not be able to form a perfect triangle (the space between 3 spherical particles with touching edges). Another reason for this increase in the flux values is due to the higher resistance to compression of the silica-coated particles under the high pressure of the filtration test. The soft uncoated polymer particles are easily compressed during the filtration test (this phenomena was observed for (PSAN-*b*-PEO-*b*-PSAN) particles with PSAN core with higher T$_g$ than PBzMA (T$_g$ ~54°C) See Ref. 22). This compression would lead to reduced pore size and to the decrease in the flux value. In contrast, membranes prepared with silica coated particles are less prone to deformation under pressure.
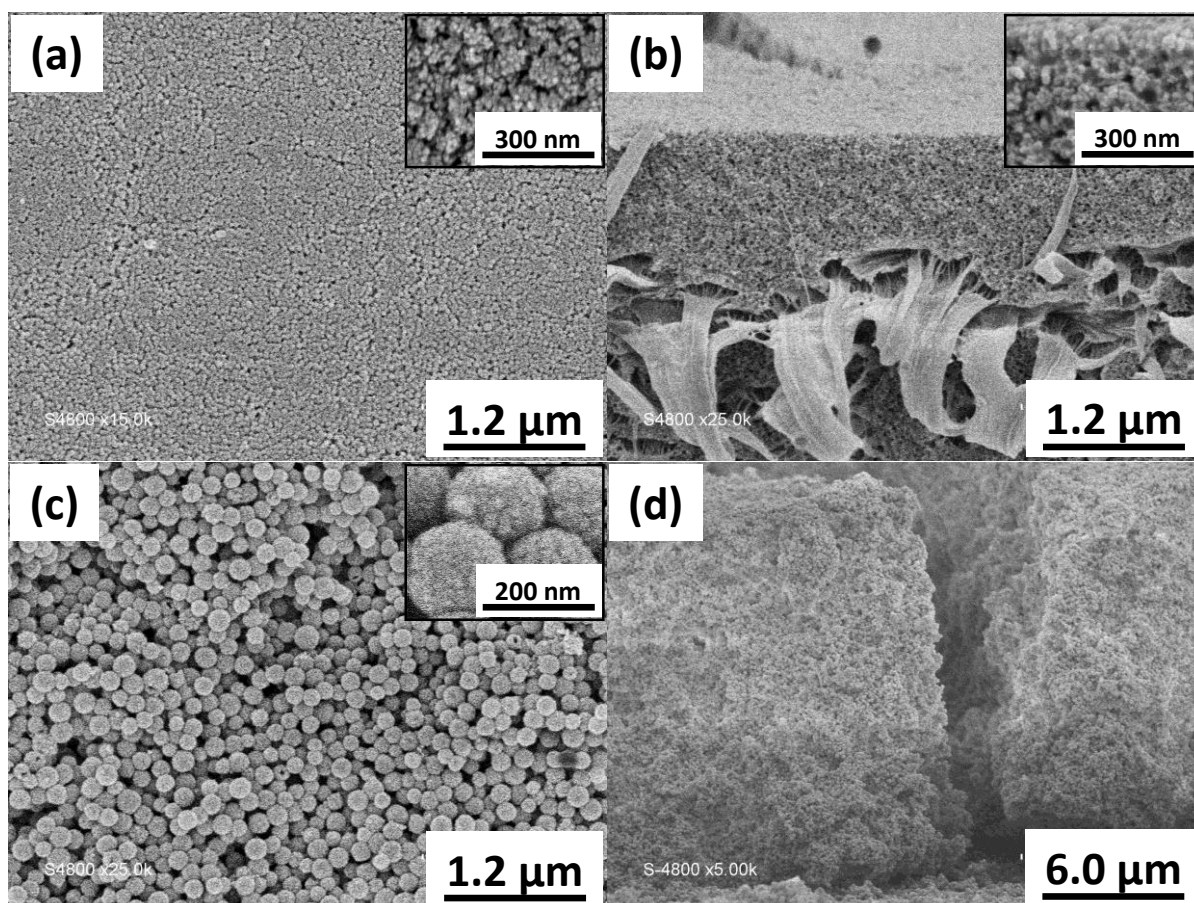
Figure 3. SEM images of thin films prepared from silica coated $PDMA_{88}$-$PBzMA_x$ diblock copolymer spheres using [TMOS]/ [diblock copolymer] of 2.5: 1 (a) film top surface x= 500 (b) film cross section x= 500 (c) film top surface x= 1000 (d) film cross section x= 1000.

All four membranes were imaged using SEM and AFM after three cycles of filtration. As shown in Figures S3, S4, S6 and S7 the arrangement of the particles in the membranes did not change and the membranes were intact after three cycles of filtration. The thin layer visible on the top surface of the membranes after filtration are due to bacteria growth since the membranes were left in water with no added preservatives (such as sodium azide solution) for several days during filtration cycles.
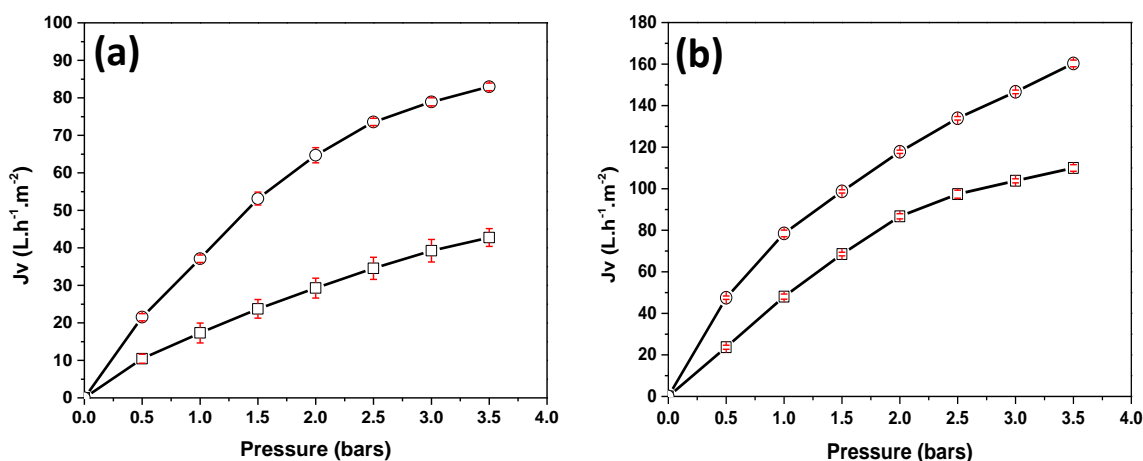
Figure 4. Water flux (Jv) obtained for membranes prepared on Nylon support using spherical particles of two different sizes (a) $PDMA_{88}$-$PBzMA_{500}$ and (b) $PDMA_{88}$-$PBzMA_{1000}$.Open squares represents naked (uncoated) spherical particles and open circles represents silica-coated particles with [TMOS]/ [diblock copolymer] of 2.5: 1.

Conclusions

In summary, a relatively long PDMA macro-CTA (DP=88) was synthesized and used to prepare a series of $PDMA_{88}$-$PBzMA_x$ spherical nanoparticles in an ethanol/ water binary mixture of 80/20 using RAFT mediated PISA. The resulting spherical particles were fully characterized using NMR, SEC, DLS and TEM. Particles formed using $PBzMA_{500}$ and $PBzMA_{1000}$ were used as templates to deposit silica sols, and form silica-coated particles. Thin film membranes were prepared from these silica-coated particles and from naked particles via spin-coating on a mechanical support (Nylon). Filtration tests at different pressures were performed and water flux values were calculated. The results suggest, as expected, that smaller spherical particles (DP_{PBzMA} = 500, 126 nm) form smaller pores compared to the particles with bigger hydrodynamic diameter (DP_{PBzMA} = 1000, 258 nm). When comparing the flux values of membranes prepared from coated and uncoated particles, it is evident that the membranes prepared from silica-coated particles display higher flux values. This may be due to the silica shell around the spherical particles that confers higher

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resistance to compression and deformation under the pressure applied during filtration tests. The presence of silica hard shell around the soft polymer particles leads to the formation of more durable and robust thin film membranes.

Supporting Information

All the diblock copolymer nanoparticle details, TEM, SEM, AFM images, SEC and DLS data are reported in the Electronic Supporting Information that is available from the Wiley Online Library.

Acknowledgements:

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Table S1. ^{1}H NMR BzMA monomer conversions, DLS intensity-average particle diameters, SEC molar mass (*Mn*) and dispersities (Đ) and TEM morphologies obtained for $PDMA_{88}$-$PBzMA_x$ synthesised at 20 % w/w solids via RAFT dispersion polymerisation of BzMA in ethanol/water mixture (80/20) at 70˚C using.

| Composition	Target DP	Conv. %	Real DP	*Mn* (gmol⁻¹)	*Mw* (gmol⁻¹)	Đ	D DLS (nm)	D TEM (nm)	Morphology
$PDMA_{88}$	90	87	88	13800	15000	1.09	-	-	-
$PDMA_{88}$-*b*-$PbzMA_{120}$	120	>99	120	27600	34500	1.25	65	26	sphere
$PDMA_{88}$-*b*-$PbzMA_{200}$	200	>99	200	36100	48200	1.34	76	32	sphere
$PDMA_{88}$-*b*-$PbzMA_{220}$	220	>99	220	39900	53400	1.34	97	52	sphere
$PDMA_{88}$-*b*-$PbzMA_{500}$	500	>99	500	74400	102500	1.38	126	88	sphere
$PDMA_{88}$-*b*-$PbzMA_{1000}$	1000	>99	1000	109000	157700	1.45	258	191	sphere
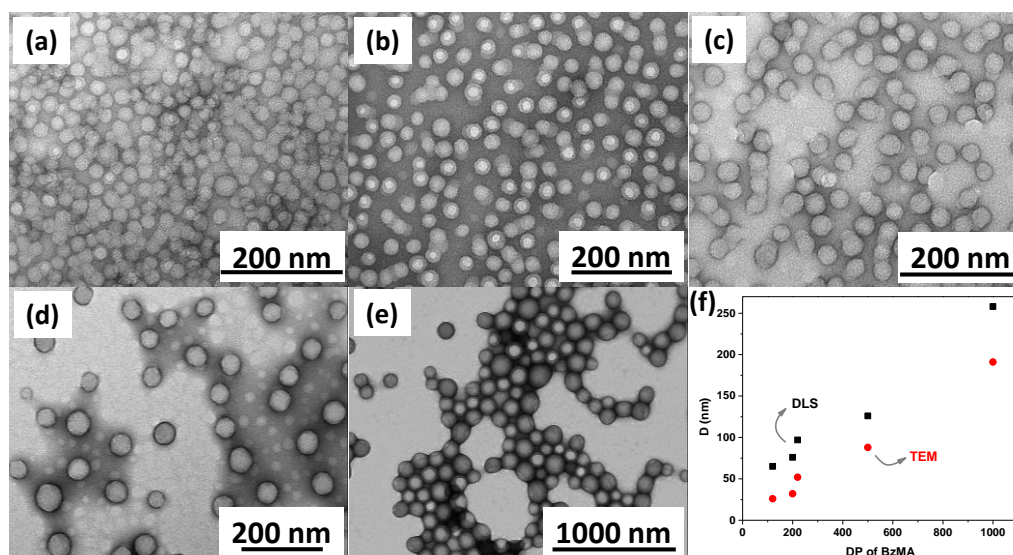
Figure S1. TEM images of $PDMA_{88}$-$PBzMA_x$ nano objects prepared via RAFT dispersion polymerisation of BzMA at 20 % w/w in ethanol/water (80/20) at 70°C using AIBN initiator

(a) x= 120 (b) x= 200 (c) 220 (d) 500 (e) 1000 and (f) the particle diameter obtained from DLS and calculated from TEM images (based on 100 particles analysed using ImageJ).

Table S2. TMOS/ diblock copolymer ratios, DLS intensity-average particle diameters, particle diameters calculated from TEM images, calculated SiO_2 shell thickness and SiO_2 mass % obtained from TGA for $PDMA_{88}$-$PBzMA_{500}$ coated with silica.

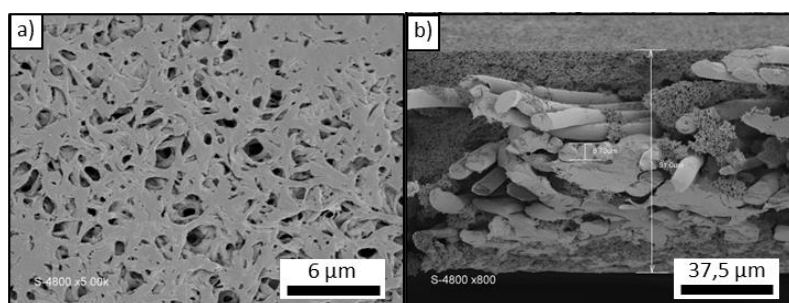| Composition	[TMOS]/[diblock copolymer]	D_{DLS} (nm)	D_{TEM} (nm)	SiO_2 thickness (measured from TEM images) (nm)	SiO_2 % (calculated from TGA)
$PDMA_{88}$-b-$PbzMA_{500}$	1.1 / 1	213	56	2	44
$PDMA_{88}$-b-$PbzMA_{500}$	2.5 / 1	216	59	4	73
$PDMA_{88}$-b-$PbzMA_{500}$	5 / 1	222	69	9	78
$PDMA_{88}$-b-$PbzMA_{1000}$	1.1 / 1	342	144	2	40
$PDMA_{88}$-b-$PbzMA_{1000}$	2.5 / 1	346	153	6	86
$PDMA_{88}$-b-$PbzMA_{1000}$	5 / 1	368	163	11	90

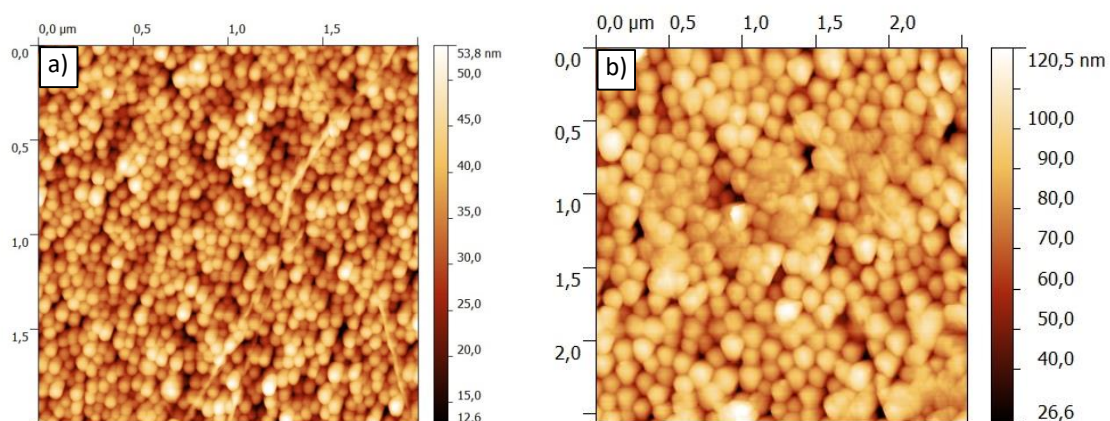**Figure S2.** SEM images of virgin Nylon support with average pore size of 0.2 μm (a) top surface (b) cross section.

Figure S3. AFM images of membrane prepared from spherical nanoparticles (a) PDMA$_{88}$-PBzMA$_{500}$ and (b) PDMA$_{88}$-PBzMA$_{1000}$ after 3 cycles of filtration (1 cycle = increasing pressure up to 3.5 bar and then decreasing to 0).
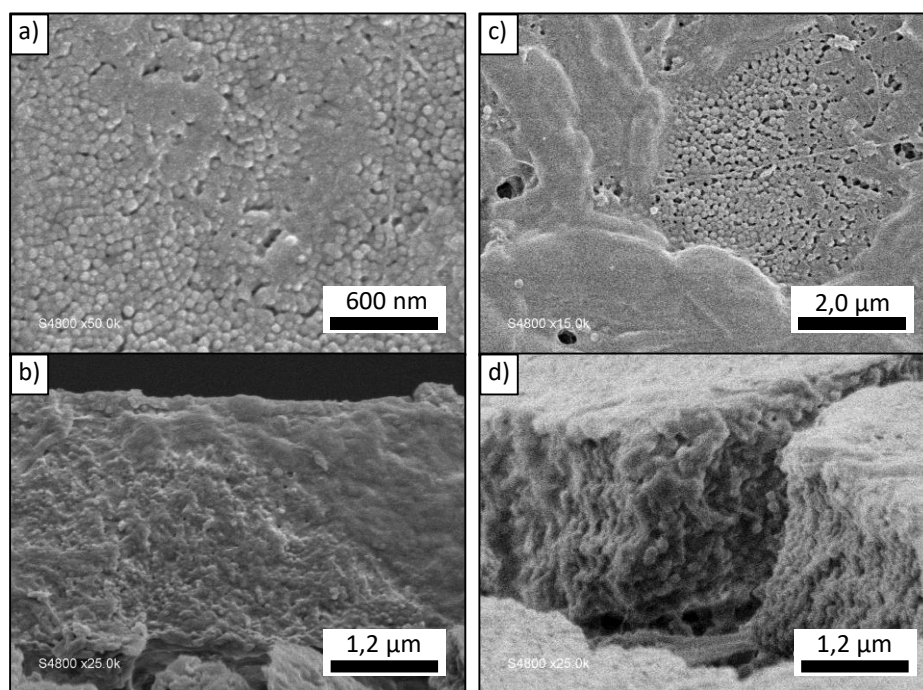
Figure S4. SEM images of membrane prepared from spherical nanoparticles (a) PDMA$_{88}$-PBzMA$_{500}$ top surface (b) PDMA$_{88}$-PBzMA$_{500}$ cross section (c) PDMA$_{88}$-PBzMA$_{1000}$ top surface (d) PDMA$_{88}$-PBzMA$_{1000}$ cross section after 3 cycles of filtration (1 cycle = increasing pressure up to 3.5 bar and then decreasing to 0).
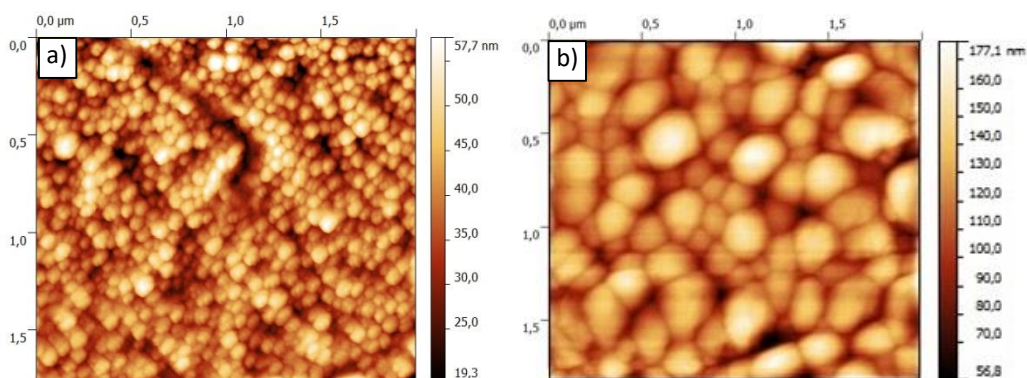
Figure S5. AFM images of membrane prepared from silica-coated ([TMOS]/ [diblock copolymer] of 2.5: 1) spherical nanoparticles (a) $PDMA_{88}$-$PBzMA_{500}$ and (b) $PDMA_{88}$-$PBzMA_{1000}$ before filtration.
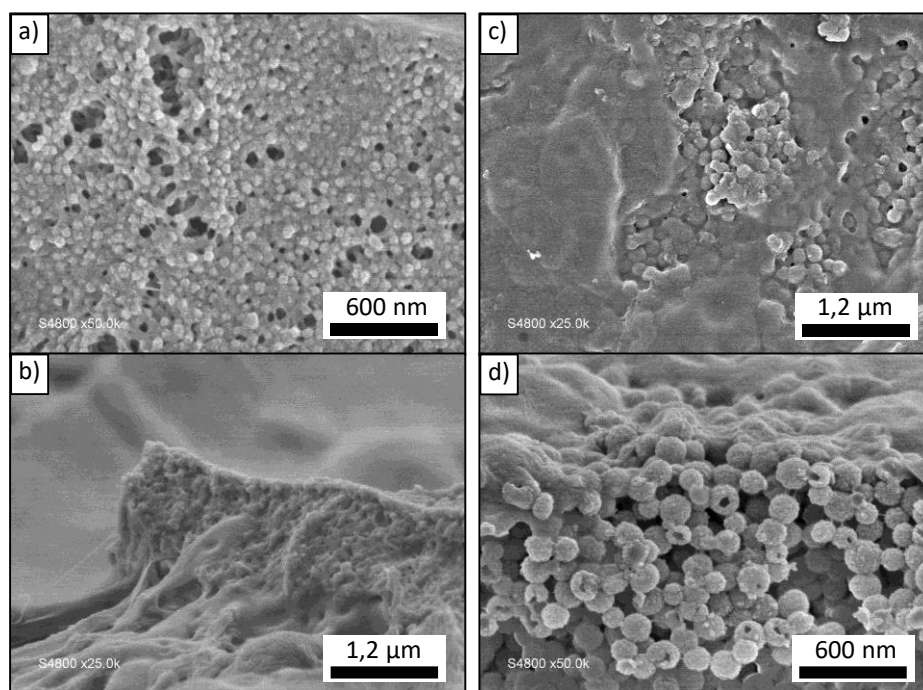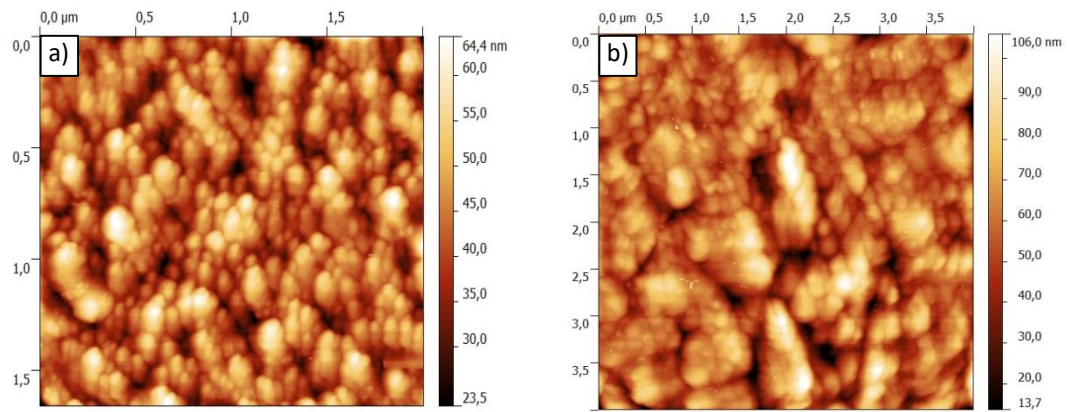

Figure S6. SEM images of membrane prepared from silica-coated ([TMOS]/ [diblock copolymer] of 2.5: 1) spherical nanoparticles (a) $PDMA_{88}$-$PBzMA_{500}$ top surface (b) $PDMA_{88}$-$PBzMA_{500}$ cross section (c) $PDMA_{88}$-$PBzMA_{1000}$ top surface (d) $PDMA_{88}$-$PBzMA_{1000}$ cross section after 3 cycles of filtration (1 cycle = increasing pressure up to 3.5 bar and then decreasing to 0).

Figure S7. AFM images of membrane prepared from silica-coated ([TMOS]/ [diblock copolymer] of 2.5: 1) spherical nanoparticles (a) PDMA$_{88}$-PBzMA$_{500}$ and (b) PDMA$_{88}$-PBzMA$_{1000}$ after 3 cycles of filtration (1 cycle = increasing pressure up to 3.5 bar and then decreasing to 0).

Eq (1):

Flux (J_v)=V_P / (t*S) (L. h^{-1}.m^{-2})

Permeability (L_P)= J_v / ΔP (L. h^{-1}.m^{-2}.bar^{-1})

TOC

Nanostructured Membranes from Soft and Hard Nanoparticles Prepared via RAFT mediated PISA

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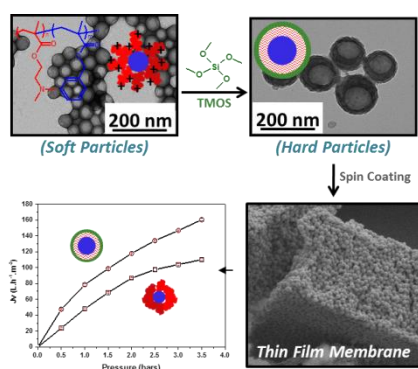
PISA prepared spherical nanoparticles of different size were used as templates for silica deposition through sol-gel using TMOS as precursor. These naked (soft) and silica-coated (hard) nanoparticles were used to prepare thin film porous membranes via spin-coating. The porous nature and performance of the resulting membranes were evaluated using imaging techniques and water flux experiments.