

Academic year 2015-2017

Erasmus Mundus Master in Membrane Engineering

www.em3e-4sw.eu

Master Thesis

**Magneto-Responsive Nano Structured Membranes from Block Copolymer
Particles**

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June 21th 2017

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The EM3E Master is an Education Programme supported by the European Commission, the European Membrane Society (EMS), the European Membrane House (EMH), and a large international network of industrial companies, research centres and universities.

The EM3E education programme has been funded with support from the European Commission. This publication reflects the views only of the author, and the Commission cannot be held responsible for any use which may be made of the information contained therein.

Table of Contents

1) Introduction:	1
1.1 Polymeric Nanoparticles:	3
1.2 Superparamagnetic NPs (SPIONs):	4
1.3 Surface Charge:	4
2) Objectives:	6
3) Characterization	6
3.1 Inorganic and Polymeric Nanoparticles Characterization:	6
3.2 Filtration tests and membrane characterization:	7
4) Result and discussion:	8
4.1 Pure Water Filtration Tests:	22
5) Conclusions	26
6) REFERENCES	27

Appendix to Thesis

APPENDIX:	I
Experimental Section:	I
Materials:	I
Inorganic NanoParticles Synthesis:	I
Synthesis of Iron oxide NanoParticles (SPIONS):	I
Functionalization of SPIONS with TPED:	II
Functionalization of SPIONS with DMSA:	III
Polymeric Nanoparticles Synthesis:	III
Synthesis Of Poly (Methacrylic Acid) Macro-Chain Transfer Agent:	III
Synthesis Of Poly (Methacrylic Acid)-Poly (Methyl Methacrylate) (PMAA₆₄-PMMA₄₀₀) Diblock Copolymer Particles:	IV
Synthesis Of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA)) Macro-Chain Transfer Agent:	IV
Synthesis Of Poly(2-(Dimethylamino)Ethyl Methacrylate- Poly(Methacrylic Acid) (PDMAEMA₈₀-PMMA₅₀₀) Diblock Copolymer:	IV
Synthesis of Poly(2-(methacryloyloxy) Ethyl Trimethyl ammonium iodide) (PQDMA) Macro- CTA Agent :	V
Cationic Block Copolymer Nanoparticle Synthesis PQDMA₂₃-PBzMA₃₀₀ via RAFT Aqueous Emulsion Polymerization:	V
Synthesis of Poly(potassium 3-sulfopropyl methacrylate) Macro-CTA:	V
Anionic Block Copolymer Nanoparticles PKSPMA₃₆-PBzMA₃₀₀ synthesis via RAFT Aqueous Emulsion Polymerization:	VI
Membrane Preparation:	VI

Table of Figures

Figure 1. Mixed matrix Membrane containing Polymeric nanoparticles and Inorganic nanoparticles[7]....	1
Figure 2. Schematic illustration of anisotropic magneto-responsive PES-based iron oxide and hydrogel mixed matrix composite ultrafiltration membrane. [12]	3
Figure 3. Schematic representation of RAFT Dispersion Polymerization of PMAA ₆₄ -PMMA ₄₀₀ and PDMAEMA ₈₀ -PMMA ₅₀₀	9
Figure 4. Schematic representation of RAFT Emulsion Dispersion Polymerization of PQDMA-b-PBzMA and PKSPMA-b-PBzMA	9
Figure 5. Schematic illustration of TPED coated SPIONs	10
Figure 6. Schematic illustration of DMSA coated SPIONs	10
Figure 7. Characterization of TPED-coated INPs, (A)- Hydrodynamic diameter by DLS, (B)- TEM photography, (C) Diameter by TEM.....	12
Figure 8. Characterization of DMSA-coated INPs, (A)- Hydrodynamic diameter by DLS, (B)- TEM photography, (C) Diameter by TEM.....	13
Figure 9. Characterization of PDMAEMA ₈₀ -PMMA ₅₀₀ (PNPs), (A) – Diameter by TEM, (B) - TEM photography.	14
Figure 10. Characterization of PMAA ₆₄ -PMMA ₄₀₀ (PNPs), (A) – Diameter by TEM, (B) - TEM photography.	14
Figure 11. TEM images of (a) cationic block copolymer nanoparticles PQDMA-b-PBzMA, and (b) anionic block copolymer nanoparticles PKSPMA-b-PBzMA	15
Figure 12. Mixed Matrix Membrane preparation via spin coating of a mixture of INPs and PMAA ₆₄ -PMMA ₄₀₀ (PNPs).....	17
Figure 13. Atomic force microscopic images of (A) PDMAEMA ₈₀ -PMMA ₅₀₀ -SPIONs-DMSA (B) PMAA ₆₄ -PMMA ₄₀₀ -SPIONs-TPED (C) PQDMA ₂₃ -PBzMA ₃₀₀ -SPIONs-DMSA (D) PKSPMA ₃₆ -PBzMA ₃₀₀ -SPIONs-TPED.	18
Figure 14. SEM images PDMAEMA ₈₀ -PMMA ₅₀₀ -SPIONs-DMSA membrane surface (A,C) Top surface before filtration (B,D) Top surface after filtration (E) cross section before filtration (F) cross section after filtration.	19
Figure 15. SEM images PMAA ₆₄ -PMMA ₄₀₀ -SPIONs-TPED membrane surface (A,C) Top surface before filtration (B,D) Top surface after filtration (E) cross section before filtration (F) cross section after filtration.	20
Figure 16. SEM images PQDMA ₂₃ -PBzMA ₃₀₀ -DMSA-SPIONs Membrane surface (A,B) Top surface. .	21
Figure 17. SEM images PKSPMA ₃₆ -PBzMA ₃₀₀ -DMSA-SPIONs Membrane surface (A,B) Top surface. .	21
Figure 20. Water flux(J _v) of (A) PKSPMA ₃₆ -PBzMA ₃₀₀ -TPED-SPIONs and (B) PQDMA ₂₃ -PBzMA ₃₀₀ -DMSA-SPIONs Membranes.....	23
Figure 22. Permeability (P _v) of (A) PKSPMA ₃₆ -PBzMA ₃₀₀ -TPED-SPIONs and (B) PQDMA ₂₃ -PBzMA ₃₀₀ -DMSA-SPIONs Membranes.	23
Figure 21. Water flux(J _v) of (A)	24
Figure 18. Water flux(J _v) of PMAA ₆₄ -PMMA ₁₀₀ -TPED-SPIONs at pH 2,7 and 10.....	24
Figure 19. Water flux(J _v) of PDMAEMA ₈₀ -PMMA ₅₀₀ -DMSA-SPIONs at pH 2,7 and 10.	25
Figure 23. Schematic illustration of the process of SPIONs.....	II
Figure 24. Schematic illustration of the process of TPED coated SPIONs	II

Abstract:

Mixed matrix membranes having combined properties of both polymeric and inorganic materials become an integral part in separation technology. Mixed matrix membrane preparation incorporates positively charged inorganic nanoparticles (INPs) with negatively charged polymeric nanoparticles (PNPs) and in the reverse way negatively charged inorganic nanoparticles (INPs) with positively charged polymeric nanoparticles (PNPs) by use of spin coating technique. The PNPs made of poly ((methacrylic acid)-*b*-(methyl methacrylate)) and poly (2 dimethylaminoethyl methacrylate)-*b*-(methyl methacrylate)) diblock copolymers were synthesized by use of RAFT dispersion polymerization in ethanol at 70°C. In the same way cationic quaternized poly (2-(dimethylamino) ethyl methacrylate)-*b*- poly (benzyl methacrylate) and anionic poly (potassium 3-sulfopropyl methacrylate)-*b*- poly (benzyl methacrylate) were synthesized by use of RAFT emulsion polymerization in water at 70°C. The inorganic counterpart, iron oxide nanoparticles coated with [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED) and Dimercaptosuccinic acid (DMSA) were synthesized and incorporated into the membrane acting as a bridge between the oppositely charged polymeric particles (due to the presence of opposite electrostatic charges). Filtration tests were carried out by using the feed of different pH at various pressures.

1) Introduction:

Since last several decades, Polymeric membranes have played an important role in various technologies. However, there are certain limitations in several applications because of their mechanical stability and chemical resistance properties.[1] Most Reliable/Suitable alternative has been evolved by using mixed matrix membranes because they provide better mechanical properties than polymeric membranes.[2] The general method consists of the incorporation of inorganic nanoparticles in a polymeric matrix in order to build up the mixed matrix membrane. The most beneficial advantage of these hybrid membranes is that they exhibit good properties of both inorganic and organic materials, Such as mechanical stability from inorganic and flexibility, low cost and processability from the polymeric material.[3] Mixed matrix membrane has been used in a wide variety of applications such as ultrafiltration for water treatment[4], selective separation of solutes for pharmaceutical and food industry[5], drug delivery, medical filtration needs (such as dialysis) and data storage.[6]

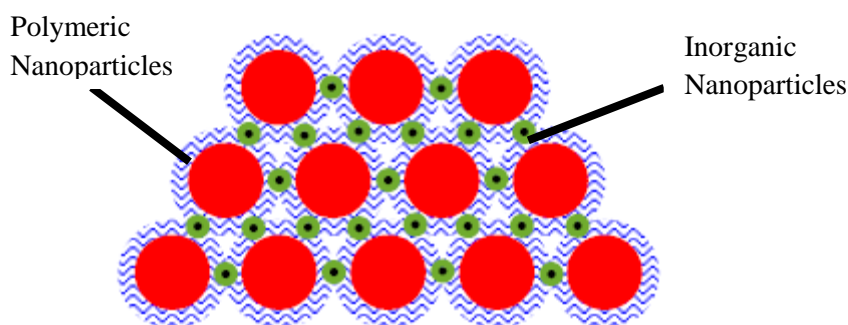


Figure 1. Mixed matrix Membrane containing Polymeric nanoparticles and Inorganic nanoparticles[7]

On the other hand, there are many inorganic nanoparticles which are being used for the mixed matrix formation depending on the applications, i.e Magnetic nanoparticles play an important role in various technologies. The main application of the mixed matrix membrane having iron oxide nanoparticles incorporated is in waste water treatment. [4] Concretely, iron nanoparticles are widely used in this field because it is well known, iron is the most available transition metal having high magnetic and catalytic activities.[8] The incorporation of the iron oxide nanoparticles increases the membrane performance with long shelf life. It has the special structure that gives rise to magnetic properties. In this way, several types of iron oxides such as magnetite Fe_3O_4 , hematite $\alpha-Fe_2O_3$, maghemite $\gamma-$

Fe₂O₃ have been used as magnetic nanoparticles. [9] Iron-based nanoparticles with diameters of up to 100 nm generate heat under alternating high frequency magnetic field due to their unique superparamagnetic behavior. Superparamagnetic NPs can be used to control effective pore diameter; due to this property they can control both transmembrane flux and size-selective exclusion of particles. Such as, Grafted chains on the magnetic nanoparticles extend during the increase of the magnetic field which decrease the pore diameter as well as also reduce the permeation of larger particles. These characteristics make a membrane a novel nanovalve. [10]

The other important term for Nanovalve membrane and other applications which discussed earlier is Stimuli-responsive membranes which have been succeeded to gain researchers interests from the past few years due to reversible switchable physicochemical properties. Stimuli-responsive membranes are able to modify the mass transfer and interfacial properties by using external stimuli such as temperature, pH, solution ionic strength, light, electric and magnetic fields. The main reason for the development of responsive membranes is that the reversible changes occur with high selectivity and at a fast rate. There are two types of stimuli-responsive membranes: [11]

- (i) Porous
- (ii) Non-Porous

Both already have a large number of established applications such as sensor, separation processes, and drug delivery devices. [11]

The changes in the conformation/polarity/reactivity of responsive polymers or functional groups in the membrane bulk or on its surfaces are the driving force of Stimuli-responsive membranes to interplay with the porous structure. The process of responsiveness in Stimuli-responsive is occurring in two steps:[11]

- (i) Use of stimuli to initiate specific conformational transitions on a microscopic level.
- (ii) Amplification of these conformational transitions into macroscopically measurable changes in membrane performance properties.

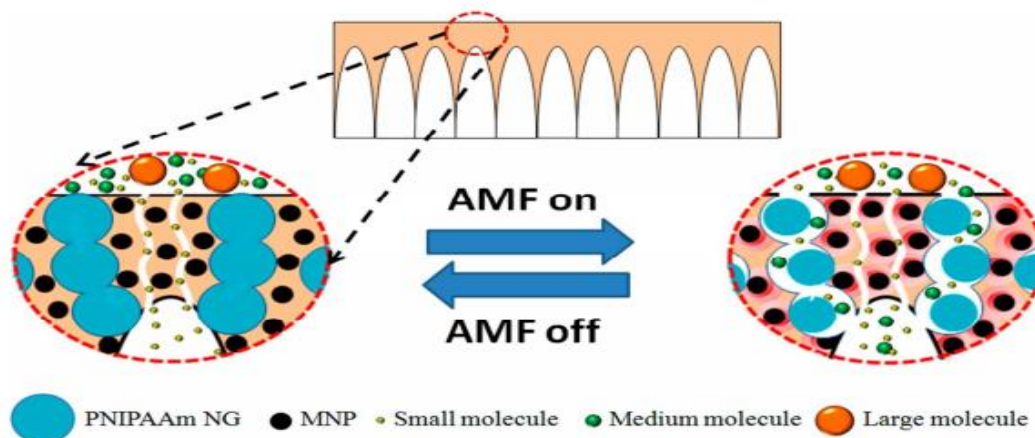


Figure 2. Schematic illustration of anisotropic magneto-responsive PES-based iron oxide and hydrogel mixed matrix composite ultrafiltration membrane.[12]

1.1 Polymeric Nanoparticles:

Polymeric nanoparticles are synthesized by reversible addition-fragmentation chain transfer (RAFT) polymerization. The RAFT polymerization is based upon the principle of rapidly reversible chain transfer. RAFT technique was first reported in 1998 in which the living character is achieved by rapidly reversible chain transfer of the propagating species using a chain transfer agent (CTA).[13] Basically, RAFT polymerization system consists of (a) a radical source, (b) monomer, (c) RAFT agent and (d) solvent. There are many advantages of RAFT polymerization such as the ability to control polymerization of a wide range of monomers polymerizable by radical polymerization, Polymerizations can be carried out in the large range of solvents (including water), within a wide temperature range, high functional group tolerance and absence of metals for polymerization. It has a significant compatibility with reaction conditions (e.g., bulk, organic or aqueous solution, emulsion, mini-emulsion, suspension) and ease of implementation and inexpensive relative to competitive technologies.[7]

1.2 Superparamagnetic NPs (SPIONs):

In relation to the synthesis of superparamagnetic NPs SPIONs, here it is worthwhile to be mentioned that there are different methods described in the literature, such as co-precipitation, sol-gel, pyrolysis, water-in-oil microemulsion, polyol, gas deposition, thermal decomposition of an organic iron precursor, and the hydrothermal method, among others.[14]

The Polyol method has been selected for the iron oxide nanoparticles synthesis for which procedure has been described in previous works of our group [15]. In this method, the reduction of dissolved iron salts and precipitation occurs in the presence of the polyol.[16] The polyols have very exceptional properties like they have a high dielectric constant, ability to dissolve inorganic compounds and high boiling temperatures and they provide a wide range of the operating temperature for the production of inorganic compounds. Polyols act as agents of reduction and as stabilizers, which make them favorable for the prevention of aggregation and control of the particles' growth.[17]

In the literature, it may find different polyols that have been used for this application, including ethylene glycol, diethyleneglycol, triethylene glycol and tetraethylene glycol. Among them, triethylene glycol has been used as polyol stabilizer in the present project due to the exceptional stability medium that provides for the nanoparticles formation, achieving non-aggregated magnetite nanoparticles with narrow size distribution and uniformed shape. [7] Triethylene glycol reacts with the iron precursor, that in our case is iron (III) acetylacetonate $[\text{Fe}(\text{acac})_3]$, also used in previous works.[15]

1.3 Surface Charge:

The surface charge of SPIONs is measured by zeta potential which is the electrical potential at the shear plane of the double layer. Zeta potential is measured by the electrophoretic mobility. SPIONs need a high zeta potential for electrostatic stabilization because aggregation and precipitation of the particles occur when zeta potential is lower than a given critical value. [18]

Moreover, the surface charge also plays an important role in transport and binding. The negative surface charge shows an increasing rejection for binding with negative membranes, therefore SPIONs surface modified with an opposite charge is the mandatory element to increase the binding strength for the different applications.[19] Surface functionalization also gives different surface charge, stability, and biocompatibility. For biomedical applications, the SPIONs surface must be covered with targeting agents, therapeutic drugs or other functional molecules.[20]

For the functionalization molecules selection, we should remember that we needed to different molecules: one that could give a positive charge to the particles, and other that would provide negative one.

In this project, a new approach was taken to prepare membranes from self-assembled amphiphilic copolymers and inorganic nanoparticles via electrostatic interaction. Oppositely charged block copolymer and inorganic nanoparticles are used to prepare thin film membranes. Previously, the group had worked on the mixed matrix membrane incorporating positively charged inorganic nanoparticles (INPs) with negatively charged polymeric particles (PNPs) using spin coating technique. The PNP of diblock copolymer were synthesized using RAFT dispersion polymerization. The inorganic iron oxide nanoparticles coated with amines were synthesized and incorporated into the membrane which is acting as a bridge between the negatively charged polymeric particles (PNPs) due to the presence of opposite electrostatic charges. The amine coated inorganic nanoparticles were paramagnetic in the previous work of group so, in this new work it is try to develop new strategies to make superparamagnetic NPs (SPIONs) having positive and negative surface charges. Along this new polymeric particles having positive and negative surface charges are synthesized as well. Thin membranes are prepared by the combination of positive inorganic nanoparticles (INP) such as SPIONS coated with [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED) and negative diblock copolymeric nanoparticle (PNP) such as PMAA₆₄-PMMA₄₀₀ and in the reverse way negative inorganic nanoparticles (INP) (SPIONs coated with Dimercaptosuccinic acid (DMSA)) and positive diblock copolymeric nanoparticle (PNP)(PDMAEMA₈₀-PMMA₅₀₀). Another set of polymeric nanoparticles having positive and negative surface charges have been prepared in

the group previously such as PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀. These particles are also mixed with inorganic nanoparticles coated with the opposite charge to prepare thin films. The aim to prepare these membranes is to use in separation technology under external magnetic field. The particles are characterized using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) to obtain the size and the morphology of the block copolymer nanoparticles. Membranes are characterized by Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Filtration Test.

2) Objectives:

Once arrived at this point and bearing in mind all the previous concepts described, we can say that the main objective of this project is to develop functionalized SPIONs and polymeric particles that could be used to build up new dynamic membranes by the assembly of the functional colloidal nanoparticles.

In order to achieve this main objective, we can divide the distribution of the present work in different sub purposes:

- Bibliographic research work for the design of the new nanomaterials.
- Selection of the SPIONs synthesis method and functionalizing molecules.
- Synthesis of cationic and anionic Inorganic nanoparticles.
- Synthesis of cationic and anionic block copolymer nanoparticles using RAFT- PISA method.
- Characterization of the prepared nanoparticles by using different techniques, before and after functionalization.
- Synthesis of membranes by the incorporation of these synthesized materials to the diblock copolymer particles by spin coating.
- Characterization of the prepared membranes by using different techniques, before and after filtration.

3) Chracterization

3.1 Inorganic and Polymeric Nanoparticles Cracterization:

NMR spectra acquired in either CDCl₃ or a mixture of CDCl₃ and (CD₃)₂SO using a Bruker 300 MHz spectrometer.

TEM studies acquired 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 aqueous polymeric and inorganic nanoparticles solution was placed onto a carbon-coated copper grid, polymeric nanoparticles (PNP) was stained using an aqueous solution of Ammonium molybdate 99.98%, and then dried under ambient conditions.

DLS and zeta potential studies were conducted using a Malvern Instruments Zetasizer Nanoseries 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 τ digital correlator electronics system. Same Malvern Instruments Zetasizer Nanoseries instrument were used to measure zeta potential solutions in presence of 10^{-3} M NaCl background electrolyte.

3.2 Filtration tests and membrane characterization:

For filtration tests, the prepared membrane ($d=2.5\text{cm}$) was fitted in a 10 mL filtration cell (Amicon 8010 stirred cell). Then the filtration cell was connected to a water reservoir and a compressed air line. The measurements were then performed at pressures between 0 and 3.5 bars. The mass of the water passing through the membrane (permeate) was recorded using 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).

Scanning Electron Microscopy (SEM) analyses were conducted using a Hitachi S-4500 instrument operating at the spatial resolution of 1.50nm at 15kV energy. The samples were dried and coated with an ultrathin layer of electrically conducting Platinum deposited by high-vacuum evaporation.

Atomic Force Microscopy (AFM) images were obtained using a Pico SPM II provided by Molecular Imaging. The imagery was controlled by the Pico View 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.

4) **Result and discussion:**

The group has previously reported the preparation of anionic and cationic diblock copolymer polymeric nanoparticles. Reversible Addition Fragmentation Chain Transfer (RAFT) aqueous dispersion and emulsion polymerization method is used to synthesize the cationic and anionic di-block copolymer particles via polymerization induced self-assembly (PISA). The cationic di-block copolymer nanoparticles synthesized by using the cationic steric stabilizer (macro-CTA) based on poly(2-dimethylaminoethyl methacrylate) (PDMAEMA), and a hydrophobic core-forming block based on Poly(methyl methacrylate) (PMMA). The other cationic di-block copolymer nanoparticles synthesized by using a cationic steric stabilizer (macro-CTA) based on quaternized poly (2-(dimethylamino) ethyl methacrylate) (PQDMA), and a hydrophobic core-forming block based on poly (benzyl methacrylate) (PBzMA). On the other hand, the anionic di-block copolymer nanoparticle is formed from an anionic steric stabilizer based on Poly(methacrylic acid) (PMAA), and a hydrophobic core-forming block based on Poly(methyl methacrylate) (PMMA). The 2nd anionic di-block copolymer nanoparticle is formed from an anionic steric stabilizer based on poly (potassium 3-sulfopropyl methacrylate) (PKSPMA), and a hydrophobic core-forming block based on PBzMA. Both block copolymers self-assembled in ethanol and water via polymerization induced self-assembly (PISA) to form spheres. The particles are characterized using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) to obtain the size and the morphology of the block copolymer nanoparticles ([Table 1](#)).

In this work the polymeric particles which we have used are the diblock copolymer of poly(2-dimethylaminoethyl methacrylate)-*b*- Poly(methyl methacrylate), Poly(methacrylic acid)-*b*- Poly(methyl methacrylate), quaternized poly (2-(dimethylamino) ethyl methacrylate)-*b*- poly (benzyl methacrylate) and poly (potassium 3-sulfopropyl methacrylate)-*b*- poly (potassium 3-sulfopropyl methacrylate).

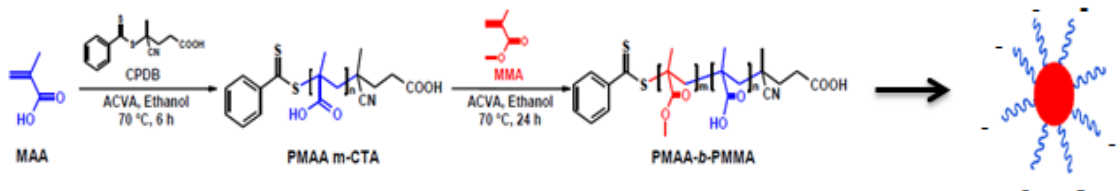


Figure 3. Schematic representation of RAFT Dispersion Polymerization of PMAA₆₄-PMMA₄₀₀ and PDMAEMA₈₀-PMMA₅₀₀

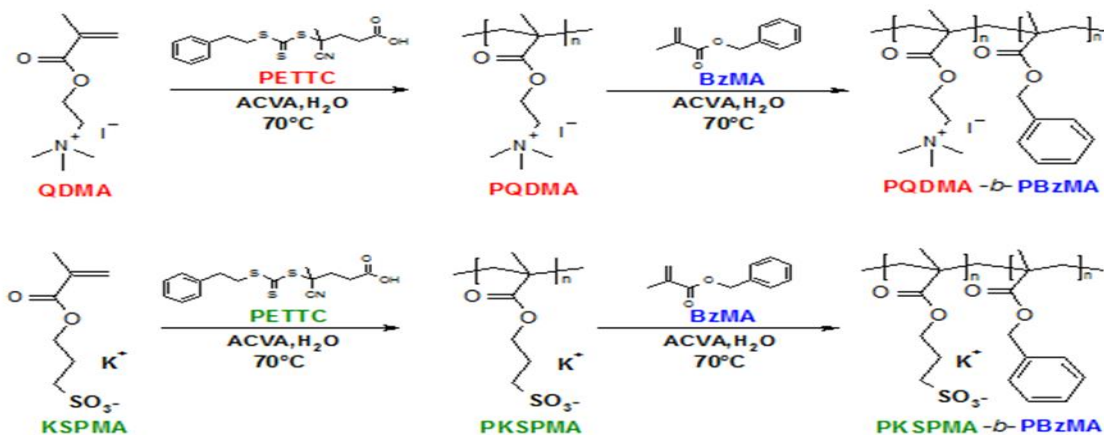


Figure 4. Schematic representation of RAFT Emulsion Polymerization of PQDMA-*b*-PBzMA and PKSPMA-*b*-PBzMA

As discussed, the inorganic nanoparticles are also coated with positive and negative charge substances so that they can interact with oppositely charged polymeric particles. Bearing this in mind, the alkoxy silanes was reacted with SPIONs via well-described reaction of silylation reaction and form a covalent Fe-O-Si, by a nucleophilic substitution reaction. One of the most commonly used alkoxy silanes is the [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED) because of the presence of three ethoxysilane sides makes it able to react easily with the nanoparticle surface. This is why we selected TPED as functionalizing molecule for the synthesis of positively charged nanoparticles. In addition, TPED has a terminal free amino group capable of further chemical modification. The amines group gives positive surface charge with high zeta potential. The zeta potential value for these particles was 23.2 ± 2.34 . (Table 1). [2]

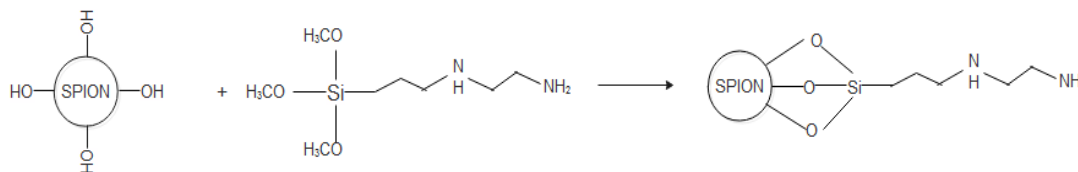


Figure 5. Schematic illustration of TPED coated SPIONs

In the reverse manner, Dimercaptosuccinic acid (DMSA) is providing an easy way to functionalize SPIONs with thiol groups. [15] Dimercaptosuccinic acid (DMSA) has been previously used in our group to achieve easily stabilized negatively charged SPIONs. [15] In this case, the DMSA is coated by a procedure of ligand exchange to disperse the colloid in water. These functionalized nanoparticles have free terminal carboxyl groups on their surface which give negative zeta potential. The zeta potential value for these particles was -25 ± 1.43 (See Table 1). The particles are characterized using Transmission Electron Microscopy (TEM) and Dynamic Light Scattering (DLS) to obtain the size and the morphology of the block copolymer nanoparticles.

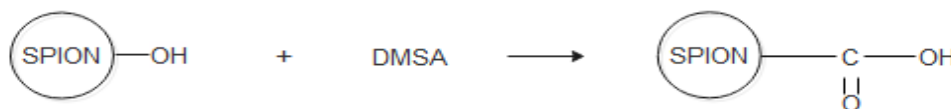


Figure 6. Schematic illustration of DMSA coated SPIONs

DLS measurements of SPIONs-TPED nanoparticles showed narrow distribution and stable spheres with an average hydrodynamic diameter of 57.4 nm. The TEM analysis of the particles suggested a diameter of 3.12 nm (Figure 7). The DLS measurements of SPIONs-DMSA also showed narrow distribution and stable spheres with an average hydrodynamic diameter of 25.4 nm while the diameter from TEM analysis was 1.02 nm (Figure 8). These nanoparticles exhibit magnetic properties of 64emu/g with a coercivity of 7.0 Oe. [7]

Table 1. Summary of particle size characterize by DLS, TEM and Zeta Potential

Sample (INPs and PNPs)	Particle size (nm)(DLS)	PDI*	Particle size(nm)±SD (TEM) n = 250	Zeta Potential
SPIONs-DMSA	25.4	0.10	1.02±1.04	-25±1.43
SPIONs-TPED	57.4	0.10	3.12±0.80	23.2±2.34
PDMAEMA ₈₀ -PMMA ₅₀₀	28.7	0.98	25.49±0.27	28.9± 5.02
PMAA ₆₄ -PMMA ₄₀₀	22.7	0.45	18.9±1.11	-38 ± 2.02
PQDMA ₂₃ -PBzMA ₃₀₀	40	0.16	-	+35± 1.08
PKSPMA ₃₆ -PBzMA ₃₀₀	45	0.58	-	-43± 2.11

The diblock copolymers were fully characterized by using H NMR and GPC. The DLS measurements of PDMAEMA₈₀-PMMA₅₀₀ showed narrow distribution and stable spheres with an average hydrodynamic diameter of 28.78 ± 1.25 nm with the polydispersity of 1.0 and diameter of 25.49 ± 0.27 nm (from TEM analysis) (See Figure 9). DLS measurements of PMAA₆₄-PMMA₄₀₀ nanoparticles also showed narrow distribution, and stable spheres with an average hydrodynamic diameter of 22.75 ± 1.66 nm, the diameter of these particles from TEM analysis was about 18.9 ± 1.11 nm (Figure 10). PMAA₆₄-PMMA₄₀₀ bears the negative surface charge due to the presence of polymethacrylic acid groups on their surface with a zeta potential of -38 ± 2.02 eV at pH 8. On the other hand, PDMAEMA₈₀-PMMA₅₀₀ particles bear positive charge on the surface due to the presence of amine group on the surface. These particles had a zeta potential of 28.9 ± 5.02 mV at pH 8 (See Table 1).

DLS measurements of PQDMA₂₃-PBzMA₃₀₀ nanoparticles showed narrow distribution, and stable spheres with an average hydrodynamic diameter of 40 nm, and DLS measurements of PKSPMA₃₆-PBzMA₃₀₀ also showed narrow distribution and stable spheres with an average hydrodynamic diameter of 45 nm (Figure 11).

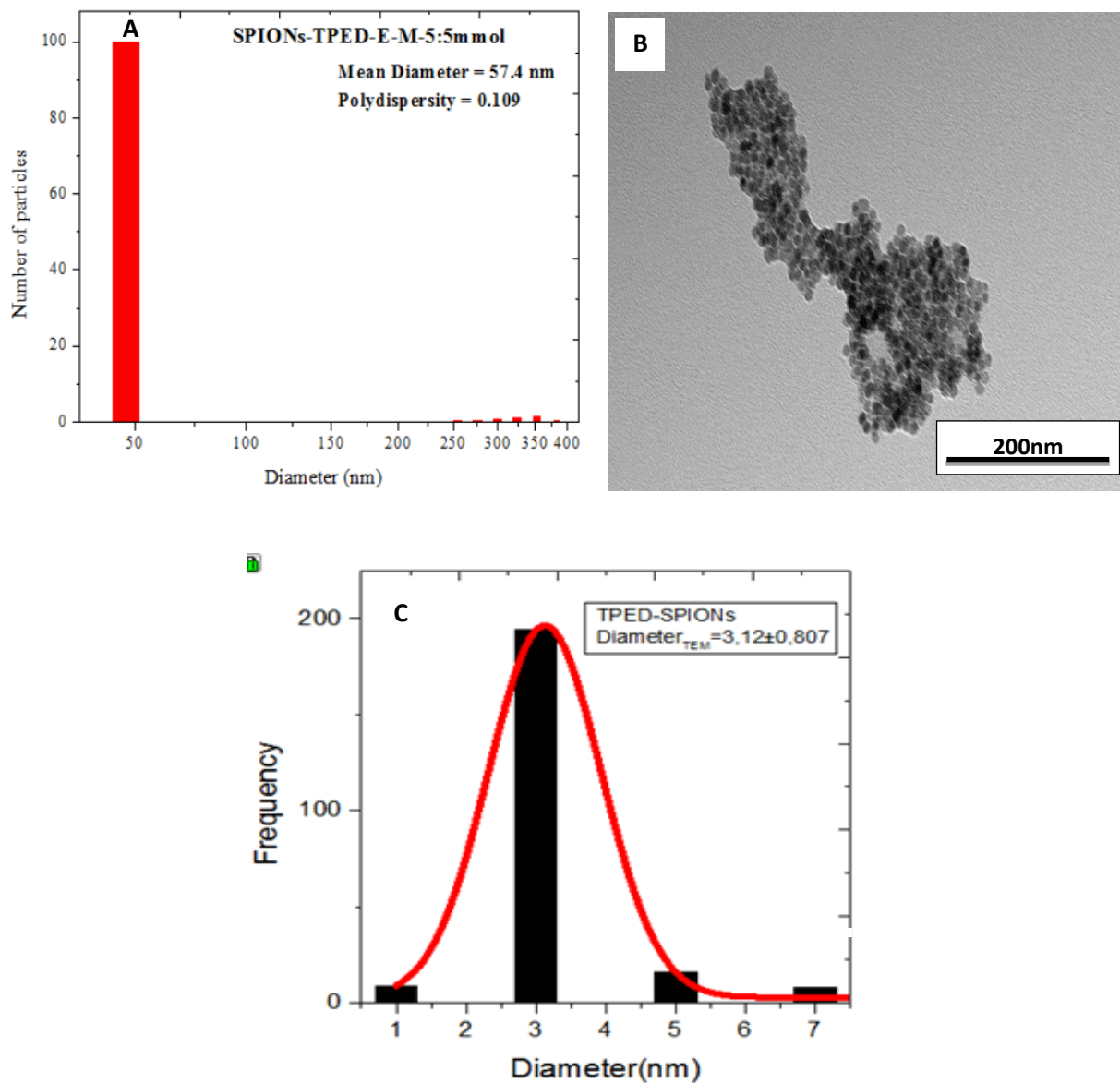


Figure 7. Characterization of TPED-coated INPs, (A)- Hydrodynamic diameter by DLS, (B)- TEM photography, (C) Diameter by TEM.

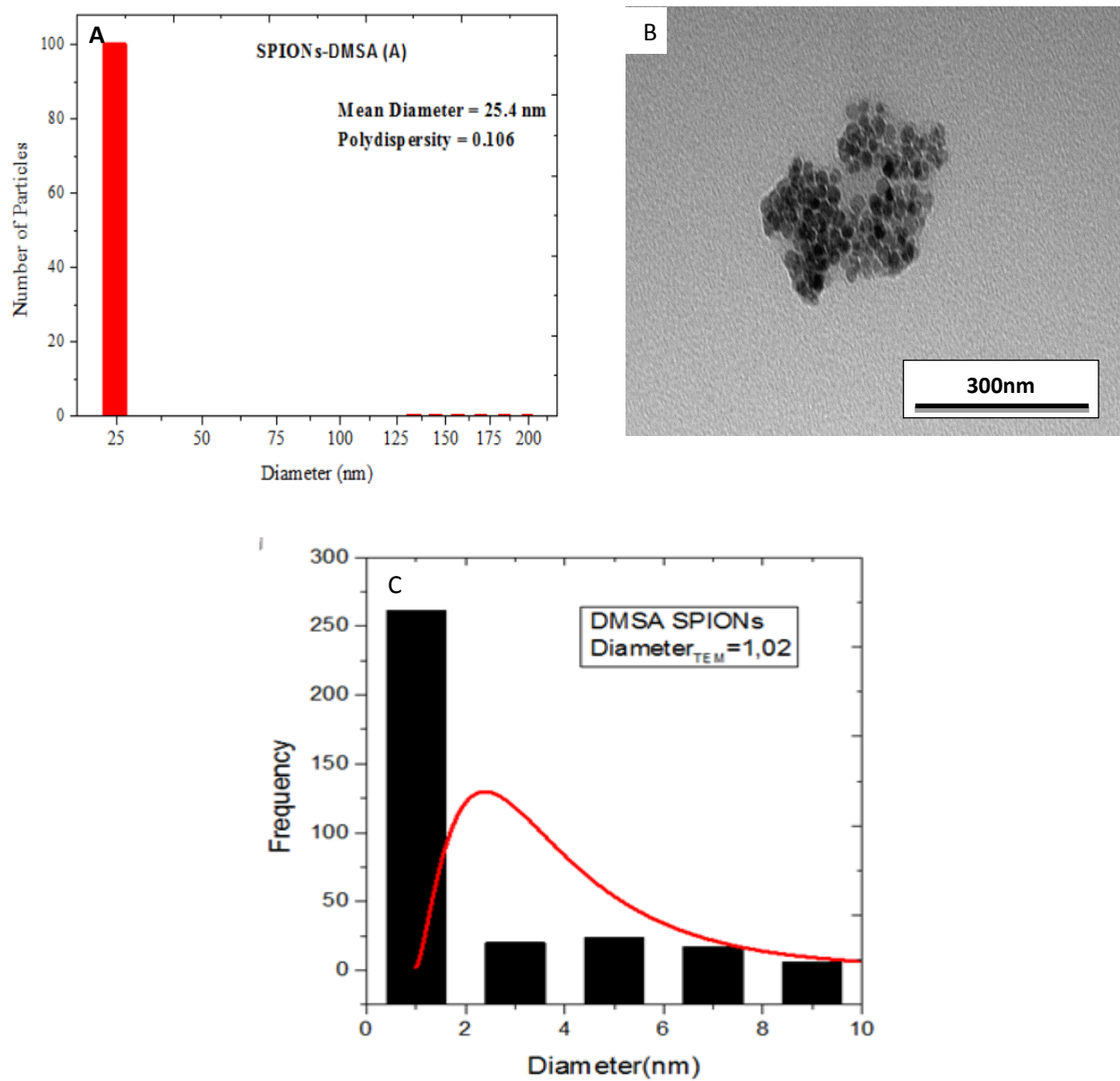


Figure 8. Characterization of DMSA-coated INPs, (A)- Hydrodynamic diameter by DLS, (B)- TEM photography, (C) Diameter by TEM.

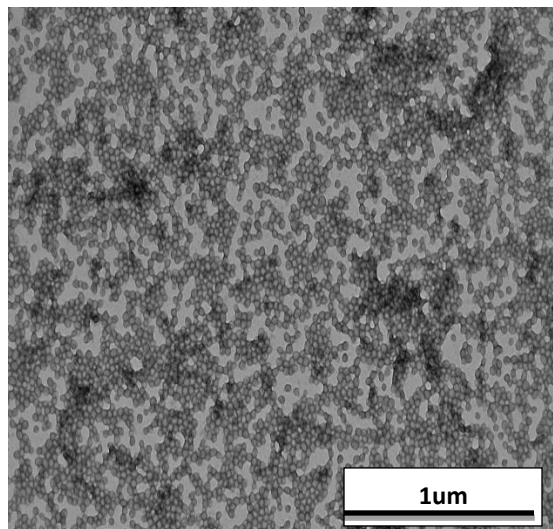
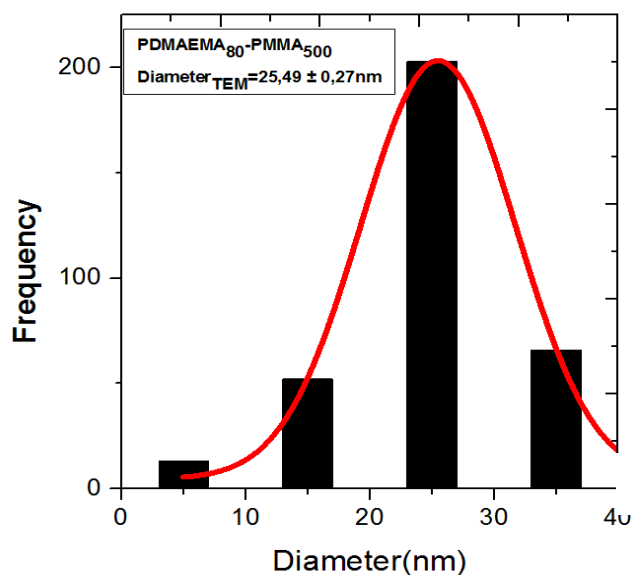


Figure 9. Characterization of PDMAEMA₈₀-PMMA₅₀₀ (PNPs), (A) – Diameter by TEM, (B) - TEM photography.

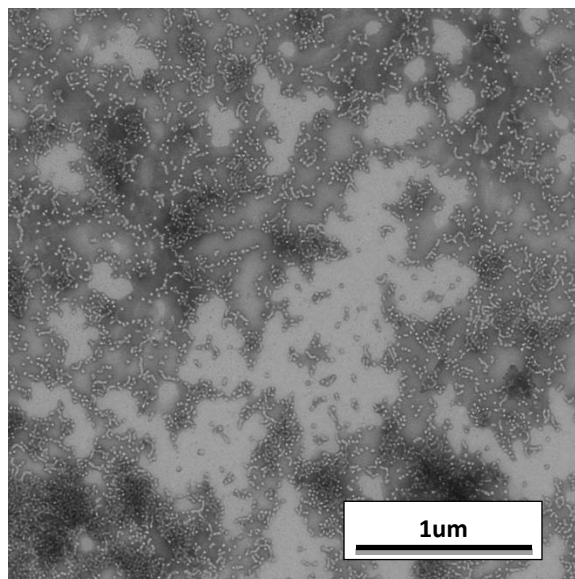
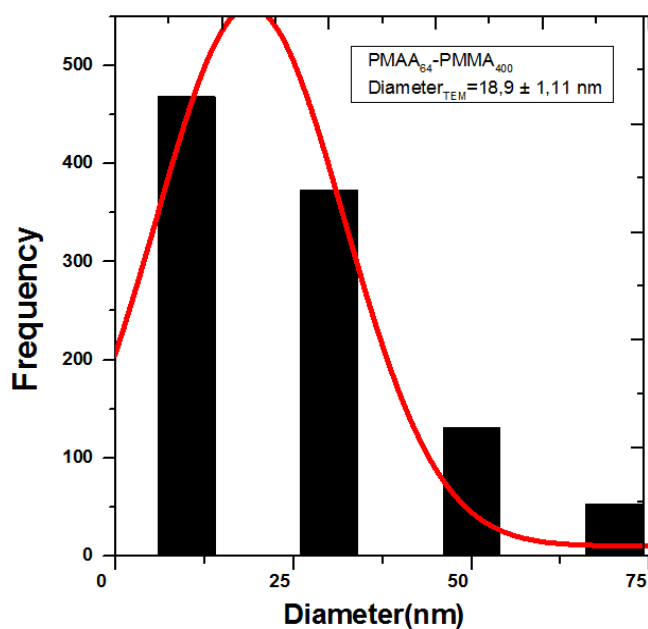


Figure 10. Characterization of PMAA₆₄-PMMA₄₀₀ (PNPs), (A) – Diameter by TEM, (B) - TEM photography.

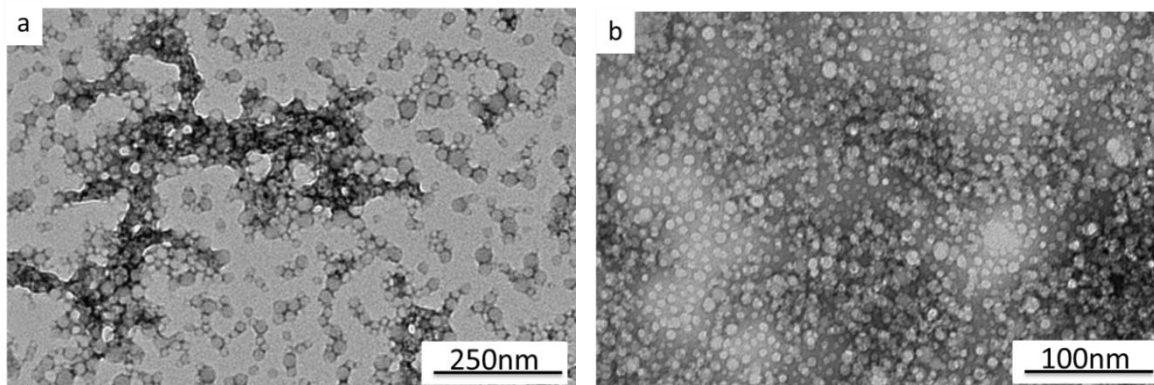


Figure 11 TEM images of (a) cationic block copolymer nanoparticles PQDMA-b-PBzMA, and (b) anionic block copolymer nanoparticles PKSPMA-b-PBzMA

Positive INPs and negative PNPs or positive PNPs and negative INPs were mixed together to prepare casting solution as discussed earlier. PMAA₆₄-PMMA₄₀₀ and PKSPMA₃₆-PBzMA₃₀₀ particles have negatively charged surface so therefore, they are mixed with positive SPIONs-TPED (INPs) while PDMAEMA₈₀-PMMA₅₀₀ and PQDMA-*b*-PBzMA have the positive charge surfaces so they are mixed with SPIONs-DMSA (INPs) which is negatively charged. Polymeric nanoparticles were synthesized in ethanol so, therefore 0.5 mL PNPs were mixed with 0.5 mL of distilled water to transfer PNPs in water followed by evaporation of the ethanol to make sure that the polymeric nanoparticles were fully charged. First PMAA₆₄-PMMA₄₀₀ and PKSPMA₃₆-PBzMA₃₀₀ (PNPs) solutions were titrated against SPIONs-TPED (INPs) solution (1.27mg/mL), to find how much INPs were needed to bridge the PNPs together. After the titration it was observed that, 1.4mL (1.27 mg/mL) of SPIONs-TPED (INP) was required for 0.5 mL of PMAA₆₄-PMMA₄₀₀ solution at 20 wt.% while 2.6 mL of SPIONs-TPED (INP) was required for PKSPMA₃₆-PBzMA₃₀₀ to reach the isoelectric point. The same procedure was followed for PDMAEMA₈₀-PMMA₅₀₀, PQDMA₂₃-PBzMA₃₀₀ (PNP) and SPIONs-DMSA (INP). 1mL (2.14 mg/mL) of SPIONs-DMSA was required to get the isoelectric point during titration against PDMAEMA₈₀-PMMA₅₀₀ (0.5 mL at 20wt.%) and 3 mL of SPIONs-DMSA for PQDMA₂₃-PBzMA₃₀₀. These added amounts of inorganic nanoparticles would provide the maximum number of positive charges before reaching the isoelectric point where precipitation takes place In order to prepare the casting solution 1.2mL of SPIONs-TPED was mixed with 0.5 mL of PMAA₆₄-PMMA₄₀₀ with 0.5 mL of distilled water. In the same way 2mL of SPIONs-

TPED was mixed with 0.5 mL of PKSPMA₃₆-PBzMA₃₀₀ with 0.5 mL of distilled water. On the other hand 0.8mL of SPIONs-DMSA was added to 0.5 mL of PDMAEMA₈₀-PMMA₅₀₀ PNP solution and 2.6 mL of SPIONs-DMSA was added to 0.5 mL of PQDMA₂₃-PBzMA₃₀₀ (see Table 2 for summary). It was observed that during stirring some of the magnetic particles attach to the magnet. Therefore, it is preferred to vortex the solution for 10-15 minutes before preparing a membrane by spin coater. Nylon (0.2 μm) membrane was used as a support and 1 mL of casting solution was spin coated on this support. Mixed matrix membranes were prepared using an SPS Spin 150 spin coater at 1500 rpm for 120 sec with the speed of 100 rpm.s⁻¹ under dry argon atmosphere.

Table 2. Summary of amounts of nanoparticles required for preparation of casting solutions.

Sample Membranes	Inorganic Nanoparticles (INPs)				Polymeric nanoparticles (PNPs)			
	Amount of INPs to get isoelectric point (mL)		Amount of INPs to make membrane solution (mL)		Amount of PNPs to make membrane solution (mL)			
	SPIONs-DMSA	SPIONs-TPED	SPIONs-DMSA	SPIONs-TPED	PDMAEMA ₈₀ -PMMA ₅₀₀	PMAA ₆₄ -PMMA ₄₀₀	PQDMA ₂₃ -PBzMA ₃₀₀	PKSPMA ₃₆ -PBzMA ₃₀₀
PMAA ₆₄ -PMMA ₄₀₀ -SPIONs-TPED	-	1.4	1.2	-	-	0.5	-	-
PQDMA ₂₃ -PBzMA ₃₀₀ -DMSA-SPIONs	3	-	-	2.6	-	-	0.5	-
PKSPMA ₃₆ -PBzMA ₃₀₀ -TPED-SPIONs	-	2.6	2	-	-	-	-	0.5
PMAEMA ₈₀ -PMMA ₅₀₀ -SPIONs-DMSA	1	-	0.8	-	0.5	-	-	-

The deposited layer of the mixture of INPs and PNPs forms the active separation layer while nylon support provides mechanical stability only. In case of PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀, it was observed by SEM and AFM that that some of the polymeric particles are gone through nylon support. SEM images showed polymeric particles on nylon support but not a dense layer therefore the glass support was used for obtaining better SEM and AFM images.

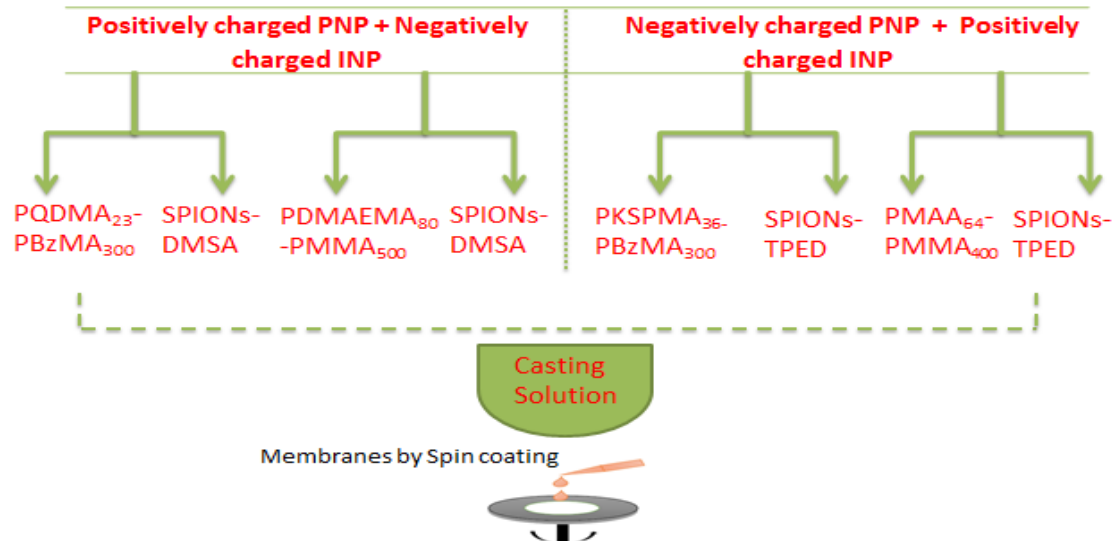


Figure 12. Mixed Matrix Membrane preparation via spin coating of a mixture of INPs and PMAA₆₄-PMMA₄₀₀ (PNPs).

The prepared membranes were analyzed by using AFM. AFM images showed the topography of the PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA (**Figure 12 (A)**), PMAA₆₄-PMMA₄₀₀-SPIONs-TPED membrane (**Figure 12 (B)**), PQDMA₂₃-PBzMA₃₀₀-SPIONs-DMSA (**Figure 12 (C)**) and PKSPMA₃₆-PBzMA₃₀₀-SPIONs-TPED (**Figure 12 (D)**). The samples showed spherical morphologies. Also, AFM confirmed that the presence of INPs was not affecting the packing of PNPs during the spin coating.

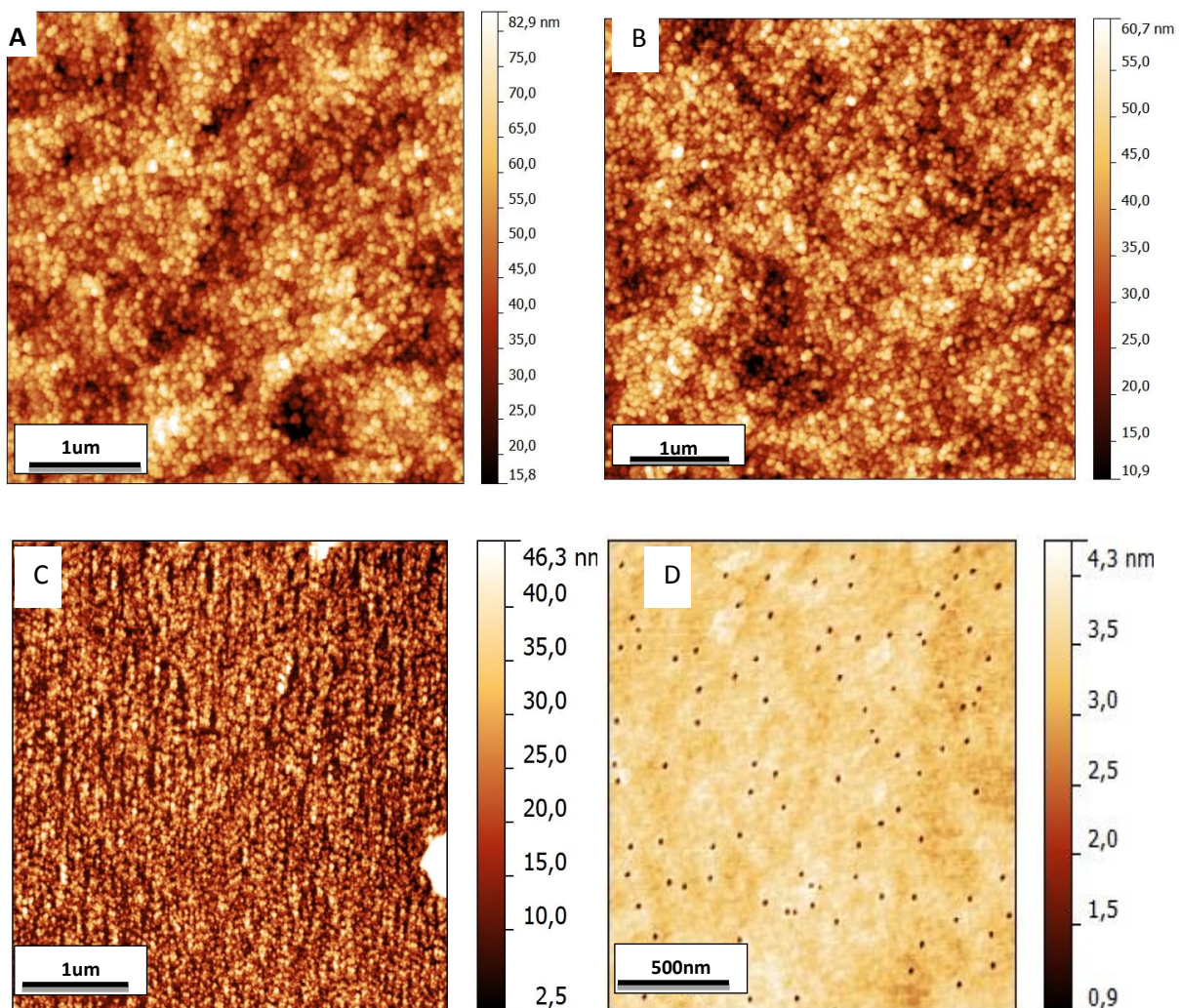


Figure 13. Atomic force microscopic images of (A) PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA (B) PMAA₆₄-PMMA₄₀₀-SPIONs-TPED (C) PQDMA₂₃-PBzMA₃₀₀-SPIONs-DMSA (D) PKSPMA₃₆-PBzMA₃₀₀-SPIONs-TPED.

The SEM images of the membranes prepared from solutions containing (1) PDMAEMA₈₀-PMMA₅₀₀ and SPIONs-DMSA (figure 13), (2) PMAA₆₄-PMMA₄₀₀ and SPIONs-TPED (figure 14) , (3) PQDMA₂₃-PBzMA₃₀₀ and SPIONs-TPED (figure 15) and (4) PKSPMA₃₆-PBzMA₃₀₀ and SPIONs-DMSA (figure 16) show no defect and the thickness of the top layer of membrane containing PMAA₆₄-PMMA₄₀₀ and SPIONs-TPED was about 1.82μm while membrane containing PDMAEMA₈₀-PMMA₅₀₀ and SPIONs-DMSA had a thickness of top layer 8.84μm .

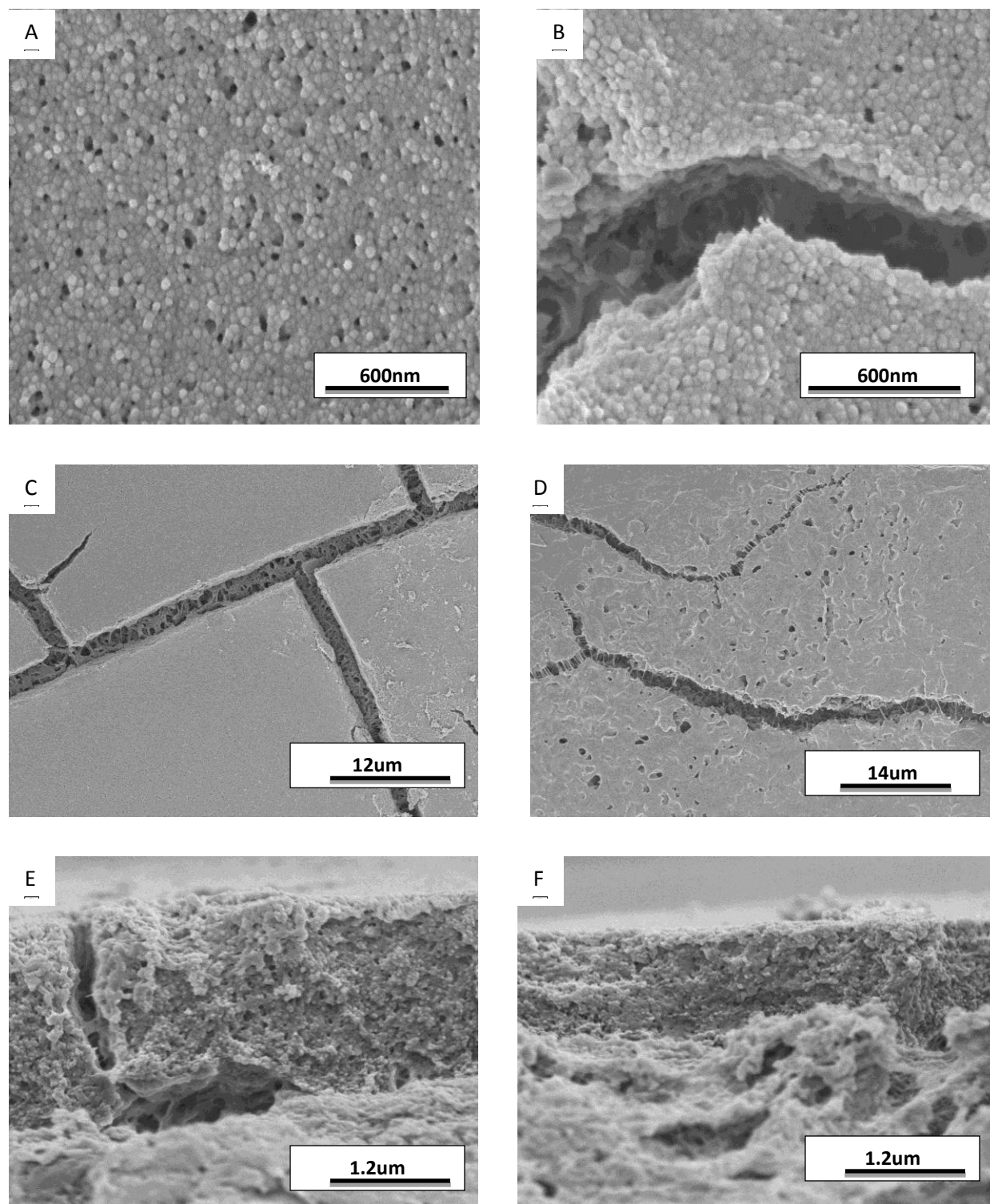


Figure 14. SEM images PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA membrane surface (A,C) Top surface before filtration (B,D) Top surface after filtration (E) cross section before filtration (F) cross section after filtration.

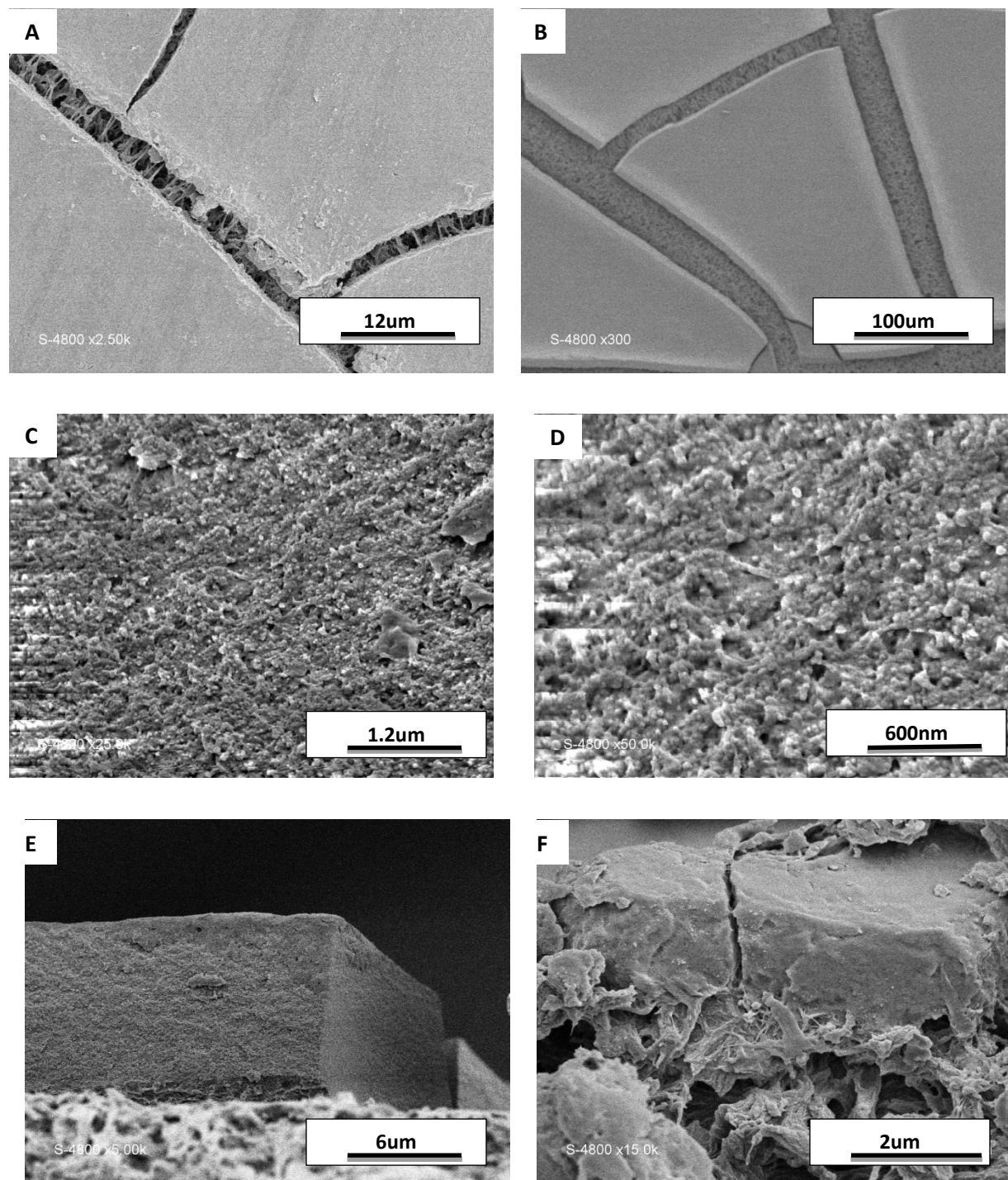


Figure 15. SEM images PMAA₆₄-PMMA₄₀₀-SPIONs-TPED membrane surface (A,C) Top surface before filtration (B,D) Top surface after filtration (E) cross section before filtration (F) cross section after filtration.

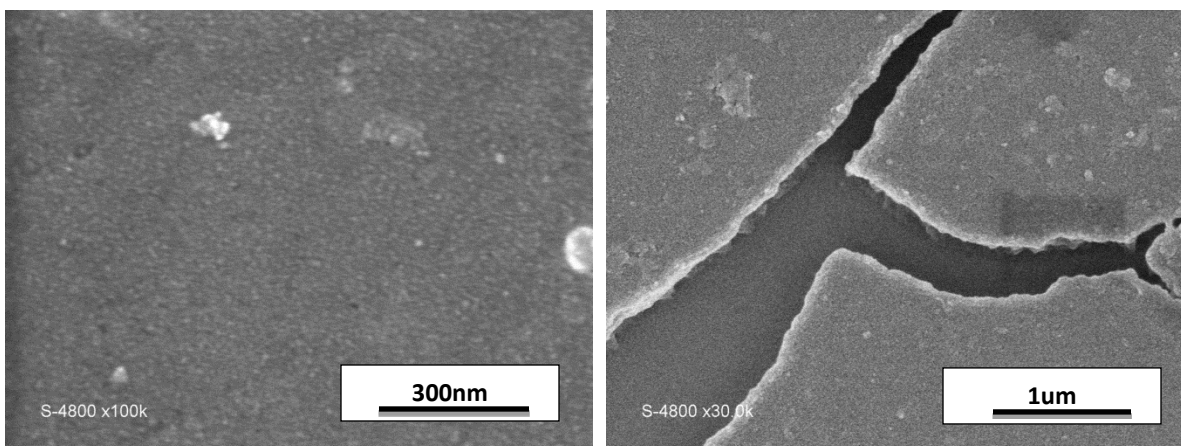


Figure 16. SEM images PQDMA₂₃-PBzMA₃₀₀-DMSA-SPIONs Membrane surface (A,B) Top surface.

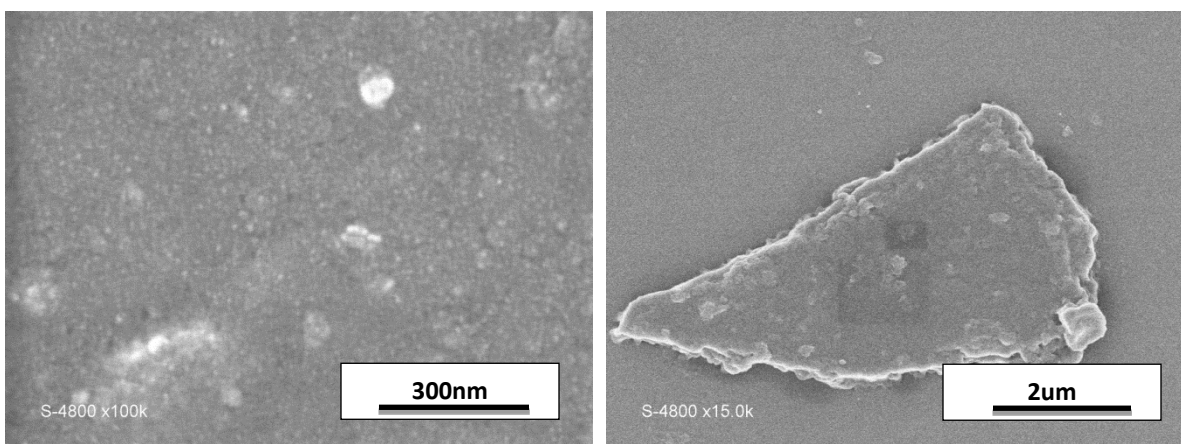


Figure 17. SEM images PKSPMA₃₆-PBzMA₃₀₀-DMSA-SPIONs Membrane surface (A,B) Top surface.

It is apparent that pores are the gaps in between the packed particles. To calculate the theoretical pore size, we employed a simple model based on the compact arrangement (hexagonal) of mono-disperse spheres.[25] Here, the diameter of the PMAA₆₄-PMMA₄₀₀ spherical particles was considered to be 18.9 nm and PDMAEMA₈₀-PMMA₅₀₀ particles was considered to be 25.5 nm which was the average diameter of the spheres. Based on the calculation that pore diameter is 0.4142 times of the sphere diameter, the estimated pore size for PMAA₆₄-PMMA₄₀₀-SPIONs-TPED would be 7.8 nm, while for PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA would be 10.6 nm. By performing the same calculation, the estimated pore size for PQDMA₂₃-PBzMA₃₀₀-SPIONs-DMSA would be 16.6 nm, while for PKSPMA₃₆-PBzMA₃₀₀-SPIONs-TPED would be 18.6 nm.

4.1 Pure Water Filtration Tests:

The prepared membranes were used for pure water filtration. The filtration test was performed on one selected PMAA₆₄-PMMA₄₀₀, PDMAEMA₈₀-PMMA₅₀₀, PQDMA₂₃-PBzMA₃₀₀ and PKSPMA₃₆-PBzMA₃₀₀ membranes. The filtration cell was then filled with water and connected to a pressurized water reservoir to perform water filtration under pressure.

Darcy's law was employed to calculate the flux and permeability of the membrane: flux $J_v = V_p / t S$ ($L \cdot h^{-1} \cdot m^{-2}$), and Permeability $L_p = J_v / \Delta P$ ($L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$). Where, correspond to water volume going through the membrane (L), time (h), the surface of the membrane (m^2) and water pressure (bars) respectively.[24]

The membrane was compressed for 2 hours at 3.5 bars first and then water flux recorded to reach an equilibrium state. Then the water flux (J_v) was measured at different pressures from 0 bar to 3.5 bars. Each point was obtained after 20 minutes of equilibrium and 20 minutes of recording.

The SEM studies of the membranes topography and top surface after filtration reveal that there is no noticeable change in the morphology and packing of the spheres. The deposited particle layers were not removed from the nylon fibers even under the highest tested pressures. Hence, this proves that the membrane is mechanically stable (Figure 14, 15)

It could be seen that the water flux increases almost linearly with the applied pressure on both the figures. For the PDMAEMA₈₀-PMMA₅₀₀-DMSA-SPIONs membrane, at 3.5 bars the calculated flux was $50.8 L \cdot h^{-1} \cdot m^{-2}$ and the corresponding permeability was $36.2 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$. While for the PMAA₆₄-PMMA₄₀₀-TPED-SPIONs membrane, at 3.5 bars the calculated flux was $7.69 L \cdot h^{-1} \cdot m^{-2}$, and the corresponding permeability was $4.60 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$. In a same way, for PKSPMA₃₆-PBzMA₃₀₀-TPED-SPIONs at 3.5 bars the calculated flux was $18.7 L \cdot h^{-1} \cdot m^{-2}$ with the permeability of $4.52 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ and for PQDMA₂₃-PBzMA₃₀₀-DMSA-SPIONs at 3.5 bars the calculated flux was $18.3 L \cdot h^{-1} \cdot m^{-2}$ with the permeability $5.34 L \cdot h^{-1} \cdot m^{-2} \cdot bar^{-1}$ correspondingly.

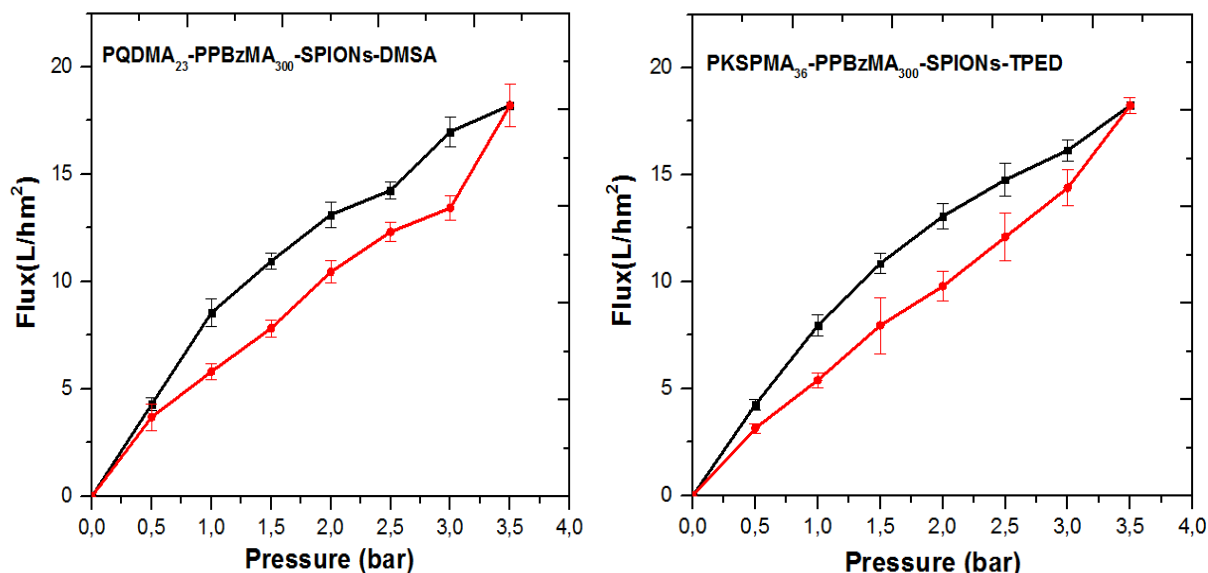


Figure 18. Water flux(J_v) of (A) PKSPMA₃₆-PBzMA₃₀₀-TPED-SPIONs and (B) PQDMA₂₃-PBzMA₃₀₀-DMSA-SPIONs Membranes.

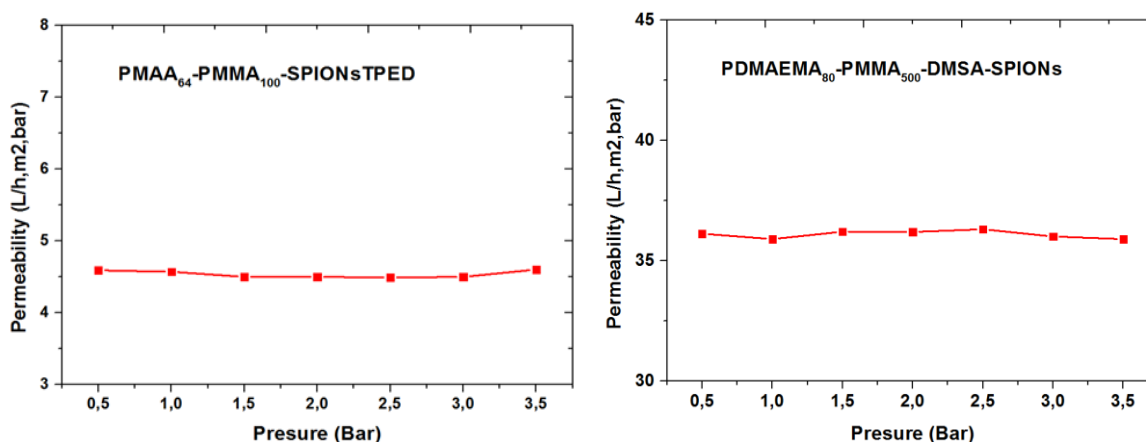


Figure 19. Permeability (P_v) of (A) PKSPMA₃₆-PBzMA₃₀₀-TPED-SPIONs and (B) PQDMA₂₃-PBzMA₃₀₀-DMSA-SPIONs Membranes.

Since the PNPs used in this work are pH sensitive. In case of PMAA₆₄-PMMA₄₀₀, it is due to the presence of PMAA on the surface (pKa = 6.1) while for PDMAEMA₈₀-PMMA₅₀₀ it is due to the presence of PDMAEMA on the surface (pKa = 7.5). Filtrations tests were carried out at different pH values. Feed solution with pH values above and below the PMAA pKa and PDMAEMA pKa (10 and 2) was selected for filtration. The flux values both at low and high pH, increases linearly with the increasing pressure (Figure 17, 18). The flux increases steadily from 3.5 L .h⁻¹.m⁻² at 1.0 bar to 34.6 L.h⁻¹.m⁻² at 3.5 bars at pH

10 for PMAA₆₄-PMMA₄₀₀-TPED-SPIONs, while for PDMAEMA₈₀-PMMA₅₀₀-DMSA-SPIONs flux increases steadily from 22.3 L.h⁻¹.m⁻² at 1 bar to 81.2 L.h⁻¹.m⁻² at 3.5 bars at pH 10. pH-responsive behavior of PDMAEMA above and below pKa, is due to deprotonation of the amine group at high pH, thereby reducing repulsion between chains and allowing for higher water permeability and flux.

The flux values are lower for PMAA₆₄-PMMA₄₀₀-TPED-SPIONs and PDMAEMA₈₀-PMMA₅₀₀-DMSA-SPIONs at pH 2. This means that there is only limited number of available negative charges to interact with the positively charged INPs at pH values below the pKa of the PMAA and PDMAEMA.

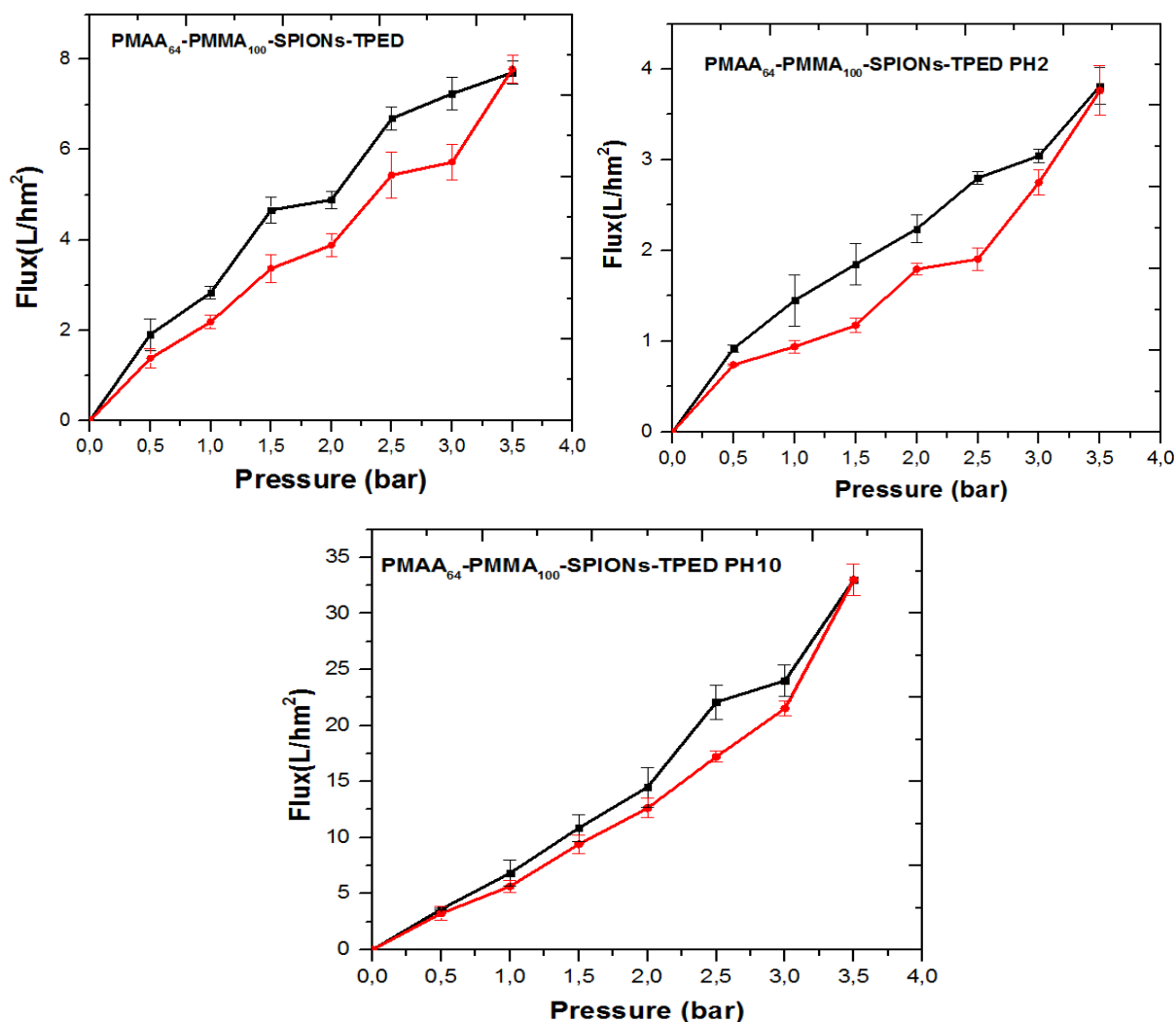


Figure 20. Water flux(Jv) of PMAA₆₄-PMMA₁₀₀-TPED-SPIONs at pH 2,7 and 10.

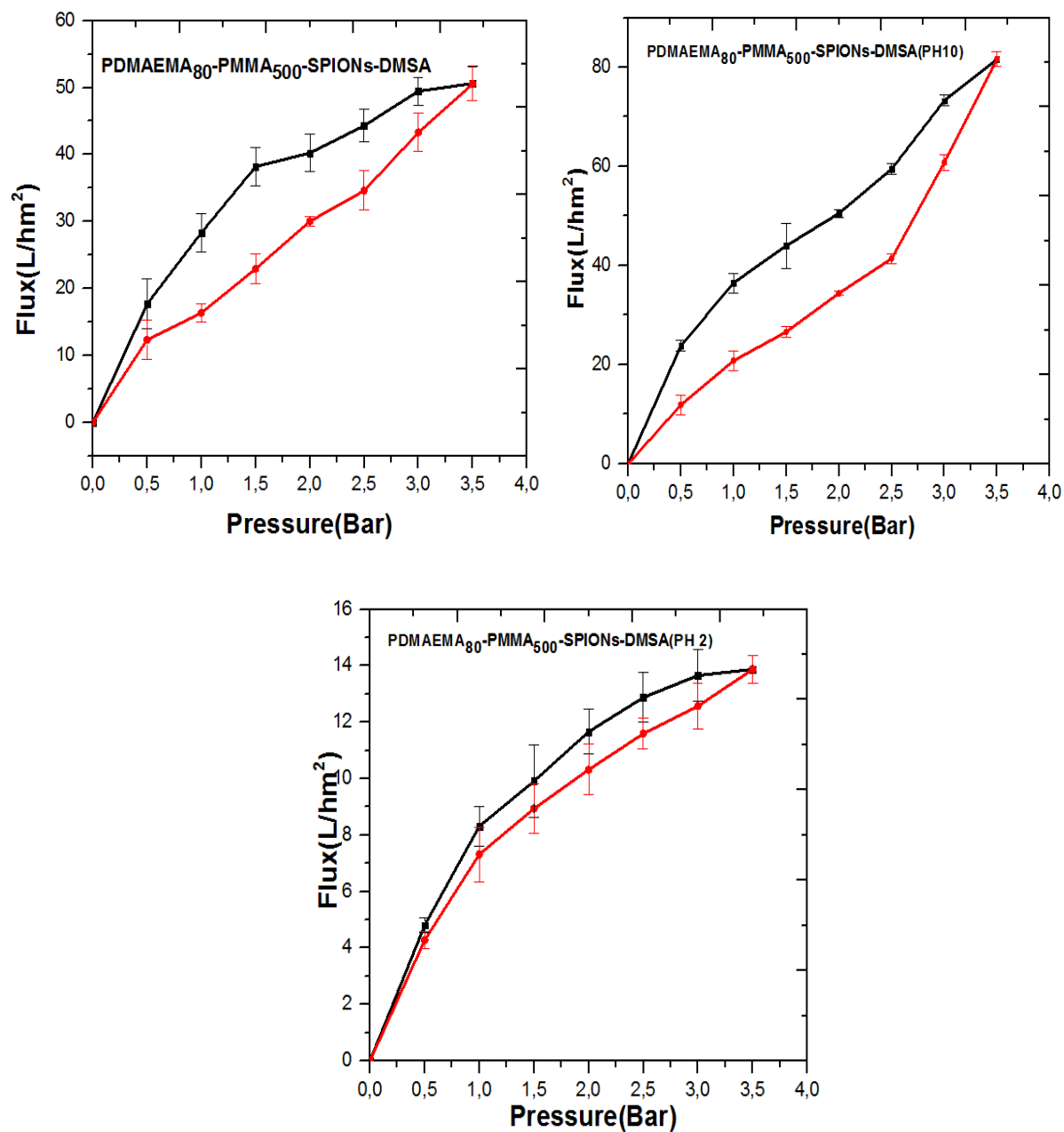


Figure 21. Water flux(Jv) of PDMAEMA₈₀-PMMA₅₀₀-DMSA-SPIONs at pH 2,7 and 10.

5) Conclusions

In this summary, superparamagnetic iron oxide nanoparticles (SPIONs) prepared by polyol method and functionalized with [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED) and Dimercaptosuccinic acid (DMSA) to achieve the positive and negative charges on their surface. PDMAEMA₈₀-PMMA₅₀₀ and PMAA₆₄-PMMA₄₀₀ synthesized via RAFT-PISA synthesis in ethanol while PKSPMA₃₆-PBzMA₃₀₀ and PQDMA₂₃-PBzMA₃₀₀ in water. High conversions achieved within 24h. DLS showed their spherical features and TEM images showed well-defined nanoparticles.

Cationic INP and anionic PNP in the reverse way, cationic PNP and anionic INP spherical particles were successfully used to prepare thin film membranes by spin coating on a nylon support film. Water filtration tests using these membranes have been carried out at different pH. Since the pKa value of polymethacrylic acid (PMAA) on the surface of PNPs is about 6.1 and for PDMAEMA on the surface is 7.5 therefore, the pH of the feed solution was varied from 2 to 10 and filtration experiments were repeated. The highest fluxes recorded were 34.3 L.h⁻¹.m⁻² and 80.5 L.h⁻¹.m⁻² for PMAA₆₄-PMMA₄₀₀-SPIONs-TPED and PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA membranes at pressure of 3.5 bars. In the case of neutral pH (7.1), the membranes PMAA₆₄-PMMA₄₀₀-SPIONs-TPED showed the flux of 7.69 L.h⁻¹.m⁻², whereas membranes PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA showed flux of 50.8 L.h⁻¹.m⁻² at 3.5 bars of pressure. In a same way, for PKSPMA₃₆-PBzMA₃₀₀-TPED-SPIONs at 3.5 bars the calculated flux was 15.4 L.h⁻¹.m⁻² and for PQDMA₂₃-PBzMA₃₀₀-DMSA-SPIONs at 3.5 bars the calculated flux was 21.3 L.h⁻¹.m⁻². When the pH was below the pKa value such as pH 2, the flux was found to be 3.76 L.h⁻¹.m⁻², 13.8 L.h⁻¹.m⁻² and 179.6 L.h⁻¹.m⁻² for membranes PMAA₆₄-PMMA₄₀₀-SPIONs-TPED, PDMAEMA₈₀-PMMA₅₀₀-SPIONs-DMSA respectively. The membrane found to have a pore size in nanometer range following lower limit of ultrafiltration and an upper bound of nanofiltration. The successful bonding of positively charged INPs to negatively charged polymeric particles (PNPs) resulted in an increased mechanical property of the final membrane. In the forthcoming work, we will explore the possible magneto-responsive behavior of these mixed matrix membranes under a magnetic field of different strengths.

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APPENDIX:

Experimental Section:

Materials:

iron (III) acetylacetonate [Fe(acac)₃] (≥97%), Triethylene glycol (TEG, 99%), Ethyl Acetate, Absolute Ethanol, [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED), meso-2,3-dimercaptosuccinic acid (DMSA) was purchased from sofma-Aldrich Spain. Methacrylic acid, Methyl methacrylate, 4-Cyano-4 (phenylcarbonothioylthio) pentanoic acid (>97%), 4,4'-azobis(4-cyanovaleric acid) (ACVA; 98%) were purchased from Sigma-Aldrich France and were used as received. NMR solvent CD₃OD was purchased from Eurisotop, Saint Aubin, France. 4-Cyano-4-(2-phenylethane sulfanylthiocarbonyl) Sulfanylpentanoic Acid (PETTC) was synthesized in IEM, Montpellier France. [26]

Inorganic NanoParticles Synthesis:

Synthesis of Iron oxide NanoParticles (SPIONs):

The synthesis of water-soluble magnetic iron oxide nanoparticles was obtained by the polyol-mediated method. Synthesis has been carried out by mixing 0.6 g of iron (III) acetylacetonate [Fe(acac)₃] vigorously with 90 mL of triethylene glycol (TREG) in a three-neck round bottom flask with a mechanical stirrer and degassed with Ar. In order to decompose the [Fe(acac)₃] precursor the resulting mixture was heated at 180°C for 30 min. After that, the mixture was heated at 280°C under reflux until it decreases to room temperature. The resulting solution cooled to room temperature. At room temperature, ethyl acetate and ethanol 40:10 mL were added to the resulting mixture for 24h. In solution, the black magnetic material was precipitated and separated by a magnetic separation with a magnetic field strength of 0.3 T. The precipitated particles was washed twice with ethyl acetate and ethanol 40:10 mL and separated with the help of a magnet. After washing the resultant product dispersed in the polar solvent such as water.[15]

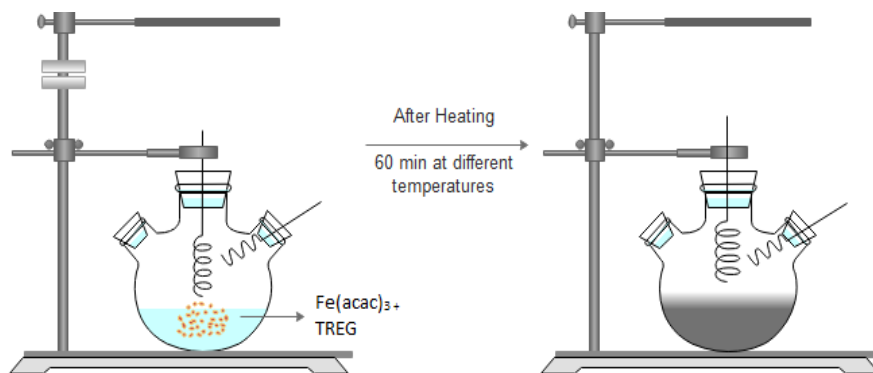


Figure 19. Schematic illustration of the process of SPIONs

Functionalization of SPIONs with TPED:

The amine-functionalized SPIONs were obtained in water medium with the different method. First 10 mL (0.05mmol) aqueous solution of SPIONs was centrifuged for 15 minutes and then separated particles was mixed in 0.02 mL (0.05mmol) of [3-(2-Aminoethylamino)propyl] trimethoxysilane (TPED) and stirred for 24 hours in 20mL of water at room temperature. After 24 hours the resulting solution was separated by the magnet and washed one time with 20 mL of water. [22]

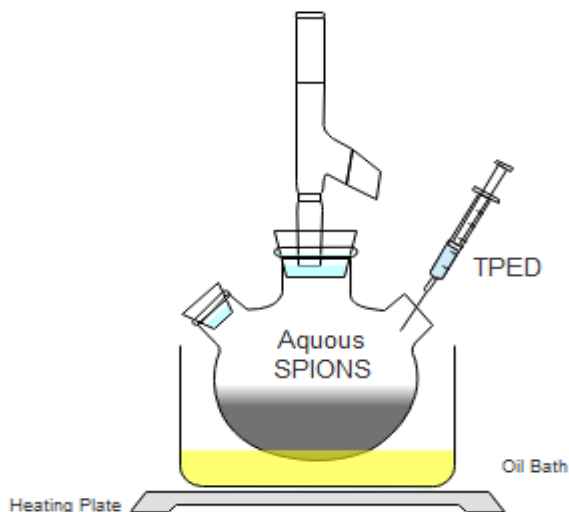


Figure 20. Schematic illustration of the process of TPED coated SPIONs

Functionalization of SPIONS with DMSA:

DMSA-SPIONS were obtained via a ligand-exchange reaction process. Two solutions were prepared separately. A DMSA aqueous solution was prepared with 25 mg of DMSA in 20 mL water. The other aqueous solution was prepared with 5 mg of NaOH in 10 mL of water. After that, add DMSA aqueous solution in separated TREG coated particles and sonicated for 5 min. After sonication, add 5 drops of NAOH solution at room temperature. The resulting mixture was immediately dialyzed for 48h by using Dialysis tubing cellulose (molecular weight cut-off = 14,000) membrane, in order to eliminate the excess DMSA. The final step was to separate dispersion by filtration through a 0.45 μm pore size filter.[15]

Polymeric Nanoparticles Synthesis:

Synthesis Of Poly (Methacrylic Acid) Macro-Chain Transfer Agent:

Semsarilar et.al [23] have previously reported the synthesis of PMAA₆₄-PMMA₄₀₀ diblock copolymer particles. A typical synthesis of PMAA macro-CTA was conducted as follows: Methacrylic acid (MAA; 5 g; 58.09 mmol), 4-Cyano-4 (phenylcarbonothioylthio) pentanoic acid (246.5 mg; 0.726 mmol), 4,4'-azobis (4-cyanovaleric acid) (203.5 mg; 0.07 mmol; CTA/ACVA molar ratio = 10.0) was dissolved in ethanol (5.0 g). The sealed vessel was purged with nitrogen for 30 minutes and placed in a pre-heated oil bath at 70 °C for 6h. The polymerization was quenched by cooling the reaction mixture to 20 °C and subsequently exposing the mixture to the air. The reaction mixture was diluted with a two-times excess of ethanol. The unreacted monomer was removed by precipitation into tenfold excess diethyl ether. The solid after precipitation was dried under vacuum for 24 h. HNMR spectroscopy indicated a mean degree of polymerization of 64. for the PMAA macro-CTA (calculated by comparing the integrated signals due to the aromatic protons at 7.2-8.0 ppm with those due to methacrylic acid backbone at (0.4 to 2.5 ppm).

Synthesis Of Poly (Methacrylic Acid)-Poly (Methyl Methacrylate) (PMAA₆₄-PMMA₄₀₀) Diblock Copolymer Particles:

A typical ethanolic RAFT dispersion polymerization synthesis of PMAA₆₄-PMMA₄₀₀ diblock copolymer at 20 % w/w solids was carried out as follows: Methyl methacrylate (MMA; 3000 mg; 2.9 mmol), AIBN initiator (3.69 mg; 0.02247 mol), and PMAA₆₄ macro-CTA (412.7 mg; 0.07491 mmol) were dissolved in ethanol (17082 mg). The reaction mixture was sealed in a 10 mL round bottom flask and purged with N₂ for 30 min. The reaction flask was kept in a preheated oil bath at 70 °C for 24 h (97% conversion as judged by ¹H NMR spectroscopy).

Synthesis Of poly(2-dimethylaminoethyl methacrylate) (PDMAEMA)) Macro-Chain Transfer Agent:

Semsarilar et.al (lanhgumier 2012) has previously reported the synthesis of PDMAEMA₈₀-PMMA₅₀₀ diblock copolymer particles. A typical synthesis of PMMA macro-CTA was conducted as follows: dimethylaminoethyl methacrylate (DMAEMA; 3000 mg; 19 mmol), 4-Cyano-4-(2-phenylethane sulfanylthiocarbonyl) Sulfanylpentanoic Acid (64 mg; 0.19 mmol), 4,4'-azobis (4-cyanovaleric acid) (3.1 mg; 0.019 mmol; CTA/ACVA molar ratio = 10.0) was dissolved in toluene (3 mL). The sealed vessel was purged with nitrogen for 30 minutes and placed in a pre-heated oil bath at 70 °C for 6h. The polymerization was quenched by cooling the reaction mixture to 20 °C and subsequently exposing the mixture to the air. The reaction mixture was diluted with a two-times excess of ethanol. The unreacted monomer was removed by precipitation into tenfold excess hexane. The solid after precipitation was dried under vacuum for 24 h. ¹H NMR spectroscopy indicated a mean degree of polymerization of 80.

Synthesis Of Poly(2-(Dimethylamino)Ethyl Methacrylate- Poly(Methacrylic Acid) (PDMAEMA₈₀-PMMA₅₀₀) Diblock Copolymer:

A typical ethanolic RAFT dispersion polymerization synthesis of PDMAEMA₈₀-PMMA₅₀₀ diblock copolymer at 20 % w/w solids was carried out as follows: Methyl methacrylate (MMA; 2000 mg; 19.9 mmol), AIBN initiator (1.31 mg; 0.0079 mmol), and

PDMAEMA80 macro-CTA (502 mg; 0.039 mmol) were dissolved in ethanol (12518 mg). The reaction mixture was sealed in a 10 mL round bottom flask and purged with N₂ for 30 min. The reaction flask was kept in a preheated oil bath at 70 °C for 48 h (96% conversion as judged by ¹H NMR spectroscopy).

Synthesis of Poly(2-(methacryloyloxy) Ethyl Trimethyl ammonium iodide) (PQDMA) Macro-CTA Agent :

In a typical experiment, a round-bottomed flask was charged with QDMA (2000 mg, 6.69 mmol), PETTC (113.5 mg, 0.334 mmol, dissolved in 1.0 mL of dioxane), ACVA (9.37 mg, 0.033 mmol), and pH 5.5 buffer (9.00 g). The sealed reaction vessel was purged with nitrogen and placed in a preheated oil bath at 70 °C for 6 h. The resulting PQDMA macro-CTA (QDMA conversion = 96%) was purified by dialysis against deionized water and isolated by lyophilization. A mean DP of 23 (6 880 g mol⁻¹) was calculated for this macro-CTA using ¹H NMR spectroscopy by comparing the integrated signal intensity due to the aromatic protons at 7.2–7.4 ppm with that due to the methacrylic polymer backbone at 0.4–2.5 ppm.

Cationic Block Copolymer Nanoparticle Synthesis PQDMA₂₃-PBzMA₃₀₀ via RAFT Aqueous Emulsion Polymerization:

For a typical aqueous emulsion polymerization of PQDMA₂₃-PBzMA₃₀₀ at 20% w/w solids, BzMA (6000 mg, 34.05 mmol), ACVA (6.36 mg, 0.023 mmol), and PQDMA₂₃ macro-CTA (781 mg, 0.114 mmol) were dissolved in water (33940 mg). The reaction mixture was sealed in a round-bottomed flask, purged with nitrogen for 15 min, and then placed in a preheated oil bath at 70 °C for 24 h.

Synthesis of Poly(potassium 3-sulfopropyl methacrylate) Macro-CTA:

In a typical experiment, a round-bottomed flask was charged with KSPMA (3000 mg, 12.2 mmol), PETTC (138 mg, 0.406 mmol, dissolved in 1.0 mL dioxane), ACVA (11.4 mg, 0.041 mmol), and an aqueous 1:7 acetic acid/sodium acetate buffer (4000 mg, 100 mM, pH 5.5). The sealed reaction vessel was purged with nitrogen and placed in a preheated oil bath

at 70 °C for 2 h. The resulting PKSPMA macro-CTA (96% conversion) was purified by dialysis against 9:1 water/methanol and isolated by freeze-drying overnight. The mean degree of polymerization (DP) 36 (8 868 g mol⁻¹) was calculated by ¹H NMR spectroscopy by comparing the integrated aromatic proton signals due to the PETTC chain end at 7.2-7.4 ppm to those due to the methacrylic polymer backbone at 0.4-2.5 ppm.

Anionic Block Copolymer Nanoparticles PKSPMA₃₆-PBzMA₃₀₀ synthesis via RAFT Aqueous Emulsion Polymerization:

For a typical aqueous emulsion polymerization of PKSPMA₃₆-PBzMA₃₀₀ at 20% w/w solids, BzMA (6000 mg, 34.05 mmol), ACVA (6.36 mg, 0.023 mmol), and PKSPMA₃₆ macro-CTA (1007 mg, 0.114 mmol) were dissolved in water (35060 mg). The reaction mixture sealed in a round-bottomed flask, purged with nitrogen for 15 min, and then placed in a preheated oil bath at 70 °C for 24 h.

Membrane Preparation:

In this work, as discussed before Inorganic nanoparticles (INP) such as SPIONs-TPED bears positive charge and SPIONs-DMSA (INP) are charged negatively. On the other hand polymeric nanoparticles (PNP) PMAA₆₄-PMMA₄₀₀ and PKSPMA₃₆-PBzMA₃₀₀ are charged negatively while PDMAEMA₈₀-PMMA₅₀₀ and PQDMA₂₃-PBzMA₃₀₀ are charged positively. Positive inorganic nanoparticle (INP) is mixed with negative polymeric nanoparticles (PNP) via electrostatic charges and vice versa. Also, inorganic nanoparticles (INP) are introducing some rigidity in the membranes. Polymeric nanoparticles were synthesized in ethanol so, therefore 0.5 mL PNPs were mixed with 0.5 mL of distilled water to transfer PNPs in water followed by evaporation of the ethanol to make sure that the polymeric nanoparticles were fully charged. First PMAA₆₄-PMMA₄₀₀ and PKSPMA₃₆-PBzMA₃₀₀ (PNPs) solutions were titrated against SPIONs-TPED (INPs) solution (1.27mg/mL), to find how much INPs were needed to bridge the PNPs together. After the titration it was observed that, 1.4mL (1.27 mg/mL) of SPIONs-TPED (INP) was required for 0.5 mL of PMAA₆₄-PMMA₄₀₀ solution at 20 wt.% while 2.6 mL of SPIONs-TPED (INP) was required for PKSPMA₃₆-PBzMA₃₀₀ to reach the isoelectric point. The same procedure was followed for PDMAEMA₈₀-PMMA₅₀₀, PQDMA₂₃-PBzMA₃₀₀ (PNP) and

SPIONs-DMSA (INP). 1mL (2.14 mg/mL) of SPIONs-DMSA was required to get the isoelectric point during titration against PDMAEMA₈₀-PMMA₅₀₀ (0.5 mL at 20wt.%) and 3 mL of SPIONs-DMSA for PQDMA₂₃-PBzMA₃₀₀. These added amounts of inorganic nanoparticles would provide the maximum number of positive charges before reaching the isoelectric point where precipitation takes place In order to prepare the casting solution 1.2mL of SPIONs-TPED was mixed with 0.5 mL of PMAA₆₄-PMMA₄₀₀ with 0.5 mL of distilled water. In the same way 2mL of SPIONs-TPED was mixed with 0.5 mL of PKSPMA₃₆-PBzMA₃₀₀ with 0.5 mL of distilled water. On the other hand 0.8mL of SPIONs-DMSA was added to 0.5 mL of PDMAEMA₈₀-PMMA₅₀₀ PNP solution and 2.6 mL of SPIONs-DMSA was added to 0.5 mL of PQDMA₂₃-PBzMA₃₀₀ ([see Table 2 for summary](#)). It was observed that during stirring some of the magnetic particles attach to the magnet. Therefore, it is preferred to vortex the solution for 10-15 minutes before preparing a membrane by spin coater. Nylon (0.2 μm) membrane was used as a support and 1 mL of casting solution was spin coated on this support. Mixed matrix membranes were prepared using an SPS Spin 150 spin coater at 1500 rpm for 120 sec with the speed of 100 rpm.s⁻¹ under dry argon atmosphere.