CHAPTER V

Synthesis and Characterization of Well-defined Amphiphilic Block Cooligomers by Organotellurium-Mediated Living Radical Polymerization (TERP)

5.1 Introduction

The attention of polymer chemists has focused on living/controlled radical polymerization (L/CRP) techniques in the last few years since radicals are compatible with a wide variety of polar functional groups which do not lend themselves to ionic and metal-catalyzed polymerization conditions.[1-5] L/CRP techniques such as nitroxide-mediated polymerization (NMP),[6] atom transfer radical polymerization (ATRP),[7-9] and reversible addition fragmentation chain transfer polymerization (RAFT)[10-15] have been the subject of intense research. Yamago et al. have recently pioneered organotellurium-mediated living radical polymerization (TERP)[16-19] as a novel L/CRP and studied its mechanism and kinetics in homogeneous systems (bulk, solution).[17,18] TERP provides well-defined polymers with a variety of polar functional groups via degenerative chain-transfer polymerization. The high controllability of these polymerizations can be attributed to the rapid degenerative-transfer process between the polymer-end radicals and corresponding dormant species. TERP exhibits good control over the number average molecular weight (M_n) and molecular weight distribution (MWD) for a variety of monomers, including styrenics, acrylates, methacrylates and nonconjugated monomers such as vinyl acetate, N-isopropyl acrylamide and N-vinyl-2-pyrrolidone (NVP).[19] It can also provide copolymers with well-defined structures and is tolerant to various polar functional groups. Furthermore, the versatility of TERP allows the synthesis of various AB, ABA, and ABC block copolymers starting from a single monofunctional initiator, regardless of the order of monomer addition.[17] A typical reaction by TERP is shown in scheme 1.5

However, till date, the C/LRP of vinylpyridines (VP) is still a challenging task, and has not been demonstrated by TERP. The living polymerization of VPs and their block copolymers by anionic polymerization[20-24] and more recently NMP,[25-29] RAFT,[30] and ATRP,[31-35] has been reported. Though, living anionic polymerization yields well-defined polymeric materials with very low MWD, but still it has a number of drawbacks. The necessity to work under very strict conditions such as, very high vacuum, very low temperatures and absence of even trace quantities of impurities like water and oxygen makes it highly unattractive. Moreover, the highly reactive carbanion prohibits the use of various functional groups.[36] Lokaj et al.[26] reported the homo- and copolymerization of 2-vinylpyridine with styrene by NMP but the obtained maximum conversion was 36.8% in case of homopolymerization and 42.3 % in case of copolymerization with 1.53 as its MWD. Chalari et al.[29] demonstrated NMP of 2-vinylpyridine but they obtained maximum yield of 66 % with narrow MWD and controllable molecular weight and could synthesize diblock copolymers provided P2VP was the first block.

Ramakrishnan et al.[32] employed living anionic polymerization followed by mechanism transfer to ATRP for the preparation of PS-*b*-P2VP. Yu et al.[35] in their research have shown the preparation and morphology of PS-*b*-P2VP heteroarm star copolymers synthesized by ATRP but their method also suffers a lack in control over the MWD which was rather high except for a low molecular weight diblock copolymer. Block copolymers composed of poly(2-vinylpyridine) (P2VP) and/or poly(4-vinylpyridine) (P4VP) segment(s), which contain pyridine moieties as side chains, have been used in many applications. For example, these block copolymers have been used as templates for metal complexes to prepare nanoparticles (NPs). These NP/copolymer assemblies improve the functionality of electronic, photonic, and chemical devices due to the presence of an unshared electron pair on the nitrogen atom of the pyridine ring and the resulting pH sensitivity.[37-43] In recent years, porous semiconducting materials have attracted much attention because of various applications in electronic, catalytic, and electrochemical devices such as solar cells,[44] electrocatalysts,[45] and sensors.[46,47] The only reported examples of Mesoporous TiO_2 materials were powder materials with lamellar and hexagonal mesoporous structures. In order to maximize the utility of TiO_2 materials for electronic and photonic applications, it is essential to synthesize mesoporous TiO_2 material as a thin film. Thus, mesoporous titanium dioxide films by sol-gel method were prepared from Ti (IV) isopropoxide in the presence of Poly(2-vinylpyridine-*b*-styrene) (P2VP-*b*-PS) as a template.

The present work concerns design and well defined synthesis of homopolymerization and block cooligomerization of 2-vinylpyridine with styrene and vice-versa (Scheme 5.1) for the first time via TERP in a controlled fashion by sequential addition of the monomers. For both homo- and block cooligomerizations a good agreement between the theoretical and experimental molecular weights was found. Molecular weight distributions for all the samples ranged between 1.10-1.24, which is well below the theoretical lower limit of 1.50 for a conventional free radical polymerization.

5.2 Experimental

5.2.1. Materials

Ethyl-2-bromoisobutyrate (Aldrich, 98%), Tellurium, powder (Aldrich, -200 mesh, 99.8% metal basis), Methyllithium (Aldrich, 1.6 M soln. in Diethyl ether) were used as such. Ethyl-2-methyl-2-methyltellanyl-propionate was synthesized according to the published procedure.[17] The monomers styrene (St) (Aldrich, 99%) and 2VP (Aldrich, 97%) were passed through activated alumina and were dried for 24 h over calcium hydride and finally distilled under reduced pressure. 2,2'-azobisisobutyronitrile (AIBN, Acros, 98%), was recrystallized from methanol, tetrahydrofuran (THF, Aldrich, 99.9%), 1-methyl-2-pyrrolidinone (NMP, Aldrich, 99.5%), Titanium(IV) isopropoxide (Aldrich, 97%) used in glove box. The silicon wafer was purchased from Prolog Semicor, Ltd., Ukraine. The silicon wafer was treated piranha solution (70/30 (v/v) of concentrated H_2SO_4 and 30 % H_2O_2) before use and other reagents were commercially available and used without further treatment.

5.2.2. Methods

To determine number average molecular weight (M_n) and molecular weight distribution, (M_w/M_n) normal Size Exclusion Chromatography, (SEC) was done using Waters M 77251, M 510 with four columns (HR 0.5, HR 1, HR 3, and HR 4, Waters Styragel columns run in series). The pore size of the columns was 50, 100, 10^3, and 10^4 Å, respectively, with a refractive index detector at a flow rate of 1 mL/min. Tetrahydrofuran (THF) containing triethylamine (2%, $(C_2H_5)_3N$) was used as the elution solvent at 40 °C, and the instrument was calibrated with styrene standards, 0.889k, 4k, 10.4k, 30k, 44k and 104k (American Polymer Standards Corp.). Nuclear Magnetic Resonance (^1H NMR) spectra were measured using a JEOL JNM-LA300WB. All spectra were measured in $CDCl_3$ and the chemical shifts were referenced to tetramethysilane (TMS) at 0 ppm.

Fourier-transform infrared spectroscopy (Perkin Elmer System 2000), FT-IR was also used for confirmation of quaternization. The 3-D polymer nanoparticle arrays were characterized with a field-emission scanning electron microscope (FE-SEM, Hitachi S-4700) at 10 kV. A field-emission transmission electron microscope (FE-TEM, JEOL JEM-2100F) operating at 200 kV was used for observing the nanoparticles. The TEM sample was prepared by dropping a polymer solution onto carbon coated copper grid and drying at 60 °C. Before measurement, P2VP-*b*-PS was stained with I_2 vapor for 10 h. Elemental analysis was performed by an energy dispersive spectrometer (EDS) attached to the FE-SEM.

5.2.3. Synthesis of TERP Promoter, Ethyl-2-methyl-2-methyltellanyl-propionate (MTEE)

To a suspension of tellurium metal (6.38 g, 50 mmol) in 50 mL of THF, methyllithium (34 mL, 1.6 M solution in diethyl ether, 55 mmol) was slowly added over 20 min at room temperature. The resulting mixture was stirred for 10 min until tellurium metal was completely soluble. To this solution ethyl 2-bromo-isobutyrate 10.7 g, 55 mmol) at room temperature was added and the resulting solution was stirred for 2 h. The solvent was removed under reduced pressure followed by distillation under reduced pressure to give the title compound, MTEE as red oil in 47 % yield (6.53 g, 25.3 mmol). **MTEE,** ^{1}H NMR (300 MHz, $CDCl_3$) 1.27 (t, J = 6.9 Hz, 3H), 1.74 (s, 6H), 2.15 (s, 3H, $TeCH_3$), 4.16 (q, J = 7.2 Hz, 2H). The unusual signals at 1.84 and 3.72 ppm correspond to tetrahydrofuran which was used during the synthesis of MTEE.

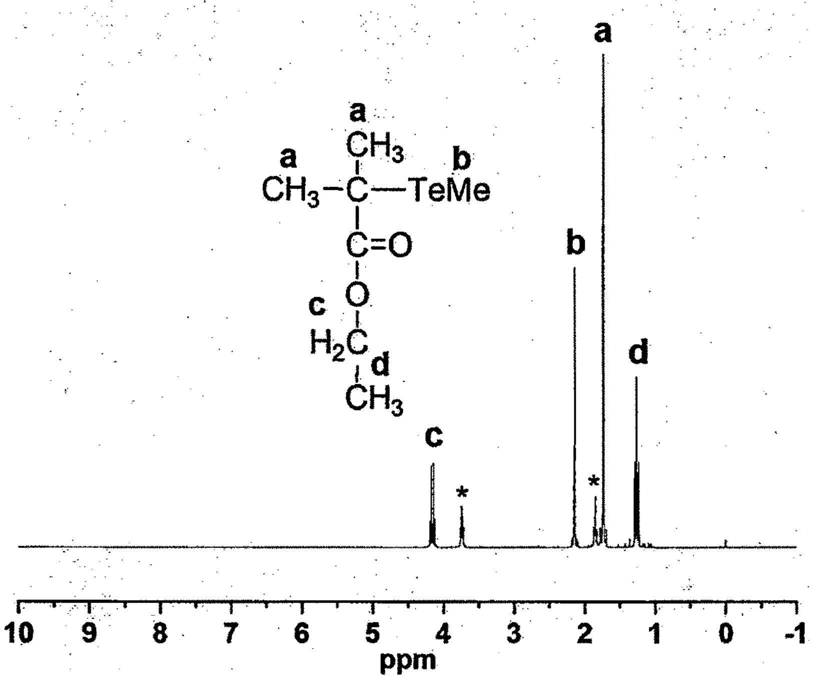
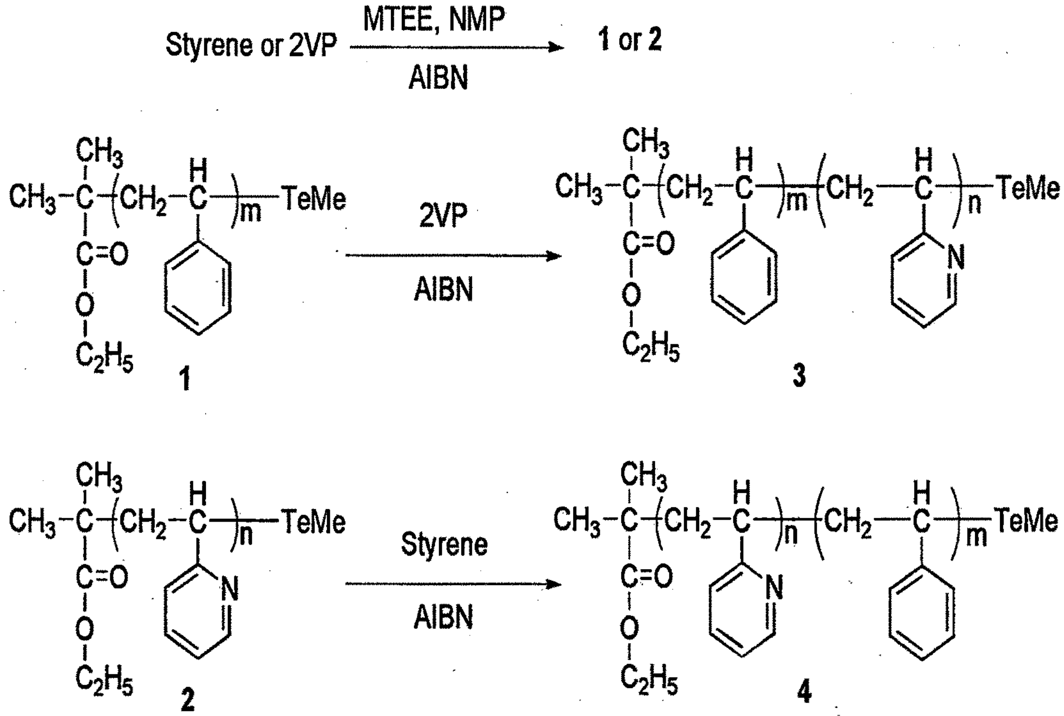


Figure 5.1. ***^{1}H NMR spectra of MTEE in $CDCl_3$, *(The signals at 1.84 and 3.72 corresponds to tetrahydrofuran).***



Scheme 5.1. Synthetic pathways for the Homo and Diblock cooligomers of Styrene and 2-Vinylpyridine at 65 °C via TERP

5.2.4. Homo- and Block cooligomerizations

5.2.4.1. Homopolymerization of Styrene (1)

Styrene (4.00 g, 38.4 mmol) and AIBN (0.150 g, 0.960 mmol) were dissolved in 5 ml of NMP, in 50 ml two-necked round-bottom flask equipped with a magnetic stirring bar and rubber septum, then the solution was deoxygenated by purging with argon for 30 min. **MTEE** (0.240 g, 0.960 mmol) was then added through a syringe which was previously flushed with argon. The polymerization was carried out at 65°C for 12 hours under argon atmosphere. At different time intervals, a small portion of the polymerization mixture was sampled out using a syringe, and subjected to measurement for molecular weights by SEC and conversion were measured gravimetrically.

5.2.4.2. Homopolymerization of 2VP (2)

2VP (9.750 g, 92.70 mmol) and AIBN (0.150 g, 0.920 mmol) were dissolved in 9 ml of NMP, in 100 ml two-necked round-bottom flask equipped with a magnetic stirring bar and rubber septum, then the solution was deoxygenated by purging with argon for 30 min. **MTEE** (0.230 g, 0.920 mmol) was then added through a syringe which was previously flushed with argon. The polymerization was carried out at 65°C for 15 hours under argon atmosphere. At different time intervals, a small portion of the polymerization mixture was sampled out using a syringe, and subjected to measurement for molecular weights by SEC and conversion were measured gravimetrically.

5.2.4.3. Block cooligomerization of styrene with 2VP (3a and 3b)

A representative example **(3a)** for the preparation of the diblock copolymer of styrene and 2VP is as follows: styrene (3.90 g, 38.00 mmol), and AIBN (0.310 g, 1.90 mmol) were dissolved in 4 ml of NMP, in 100 ml two-necked round-bottom flask equipped with a magnetic stirring bar and rubber septum, then the solution was deoxygenated by purging with argon for 30 min. To this flask, **MTEE** (0.480 g, 1.9 mmol) was added through a syringe which was previously flushed with argon. Polymerization was carried out at 65°C for 15 hours under argon atmosphere. The reaction mixture containing styrene homopolymer was sampled out and is subjected to measurement for molecular weights by SEC and conversion was measured gravimetrically. SEC and gravimetrical analysis's indicates that the M_n of the first block was 2246 with M_w/M_n of 1.12, as shown in Table 5.2 and conversion was >95% respectively.

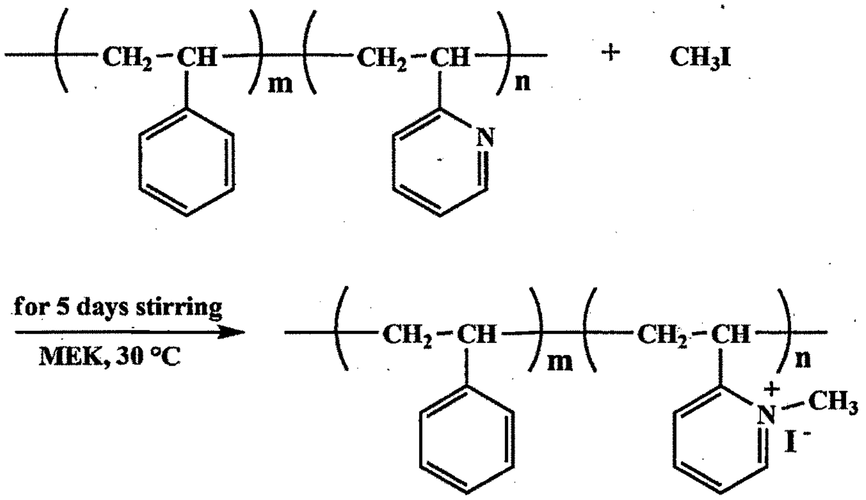
Then the second monomer, 2VP (4.00 g, 38.0 mmol) and AIBN (0.124 g, 0.760 mmol) were introduced via syringe to the flask after deoxygenating the solution with argon for 30 min. The second stage polymerization at 65°C was allowed to continue for 17 hours. After completion of the polymerization, M_n and M_w/M_n was measured by SEC and conversion by gravimetrically. The polymers were purified by reprecipitating from tetrahydrofuran into a large excess of hexane. During the synthesis of **3b**, 2VP (3.90 g, 38.0 mmol), and AIBN (0.310 g, 1.90 mmol) were added at the second stage of the polymerization.

5.2.4.4. Block cooligomerization of 2VP with Styrene (4)

A representative example (**4**) for the preparation of the diblock cooligomer of 2VP and Styrene is as follows: 2VP (4.00 g, 38.0 mmol) and AIBN (0.340 g, 2.10 mmol) were dissolved in 4 ml of NMP, in 100 ml two-necked round-bottom flask equipped with a magnetic stirring bar and rubber septum, then the solution was deoxygenated by purging with argon for 30 min. To this flask, **MTEE** (0.540 g, 2.10 mmol) was added through a syringe which was previously flushed with argon. Polymerization was carried out at 65°C for 17 hours under argon atmosphere. The reaction mixture containing 2VP homopolymer was sampled out and subjected to measurement for molecular weights by SEC and conversion by gravimetrically. SEC and gravimetrical analysis's indicates that the M_n of the first block was 1862 with M_w/M_n of 1.13, as shown in Table 5.2 and conversion was >99% respectively. Then, the second monomer, styrene (3.90 g, 38.0 mmol), and AIBN (0.520 g, 3.1 mmol) were introduced via syringe to the flask after deoxygenating the solution with argon for 30 min. The second stage polymerization at 65°C was allowed to continue for 15 hours. After completion of the polymerization, M_n and M_w/M_n was measured by SEC and conversion by gravimetrically. The polymers were purified by reprecipitating from tetrahydrofuran into a large excess of hexane.

Quarternization

For the quaternization of pyridine unit, P2VP-*b*-PS (**4**, scheme 5.1) (0.5 g) was dissolved in 50 mL of methyl ethyl ketone (MEK) and stirred for 30 min at room temperature. 5-fold excess CH_3I compared to molar ratio of the P2VP block was added to the solution. After several hours, the color of the solution changed from clear colorless to opaque light yellow solution which is an evidence of quaternization. (Scheme 5.1) After further 5 days, the reaction mixture was poured into a large amount of hexane, filtered, and dried under vacuum for 1 day.[48]



Scheme 5.2. Quarternization of poly(2-vinylpyridine) block of PS-b-P2VP.

5.3. Preparation of P2VP-*b*-PS Polymer Solution

Quaternized P2VP-*b*-PS powder (**4**, 0.0125 g) was dissolved in 10 mL toluene under vigorous stirring and sonicated for 3 days. To remove dust and large aggregated particles, the nanoparticle solution was filtered with 0.45 μm syringe membrane filter.

5.3.1. Fabrication of titania layer

Titanium(IV) isopropoxide, was mixed in ethanol (1:19 volume ratio) as a sol precursor solution for preparation of nanoporous titania layer. The sol solution was used with various amounts of 0.5~2 mL. The sol solution was infiltrated to the polymer solution prepared above. The resulting solution was subsequently aged with stirring at room temperature for 2h before gelation. The clear yellow solution can be stored at room temperature for several weeks without apparent changes.

5.3.2. Preparation of polymer/TiO_2 thin films

Thin films were obtained by spin-coating, during film deposition the substrate was rotated at 2200 rpm for 10s. As-deposited films were annealed at 150 °C for 6 hr and then heated to the 600 °C to remove the template and to increase crosslinking of the inorganic framework. After sintering, a mesoporous TiO_2 structure was obtained. Another method to remove polymer was Oxygen Plasma etching 120 Watt, 10^{-2} torr) for 20 min.[49]

5.4. Result and Discussion

5.4.1. Homopolymerization of Styrene (1)

The results for the homopolymerization are summarized in Table 4.1 good agreement between the theoretical and experimental molecular weights is observed. Figure 5.2 (a) shows the overlay of the RI traces from the SEC analysis for the homopolymerization of poly(St) (1) and clearly illustrates the increase in molecular weight with time. These elution profiles are unimodal and symmetrical which is qualitatively indicative of a controlled polymerization.

Table 5.1. Conversion, Molecular weight, and Molecular Weight Distribution Data for Homopolymerization of Styrene and 2-vinylpyridine

Sample[a] (St/2VP)	Time (h)	conv[b] (%)	M_n (theory)[c]	M_n (exp)	M_w/M_n
St1/-	2.5	35	1715	1952	1.11
St2/-	5	55	2549	2561	1.14
St3/-	7.5	75	3382	3081	1.18
St4/-	12	93	4132	4067	1.22
-/VP1	3.5	36	4042	3771	1.15
-/VP2	7.0	53	5830	5635	1.17
-/VP3	12.5	70	7617	7208	1.24
-/VP4	15	92	9930	9440	1.24

[a] Polymers synthesized at 65 °C in 1-methyl-2-pyrrolidinone (NMP) 100 vol % vs [M] under argon atmosphere with 2,2'-Azobis(2-methylpropionitrile) as the initiator and MTEE as a promoter. The molar ratio of [St]:[MTEE]:[AIBN] was 40:1:1. In case of 2VP the ratio was 100:1:1 [b] conversions were determined gravimetrically. [c] Number average molecular weight (M_n) was calculated using the relation $M_{n\,\text{theory}} = M_{n,\,\text{MTEE}} + \{[M]_0/[AIBN]_0\} \times$ Molar mass of the monomer × conversion.

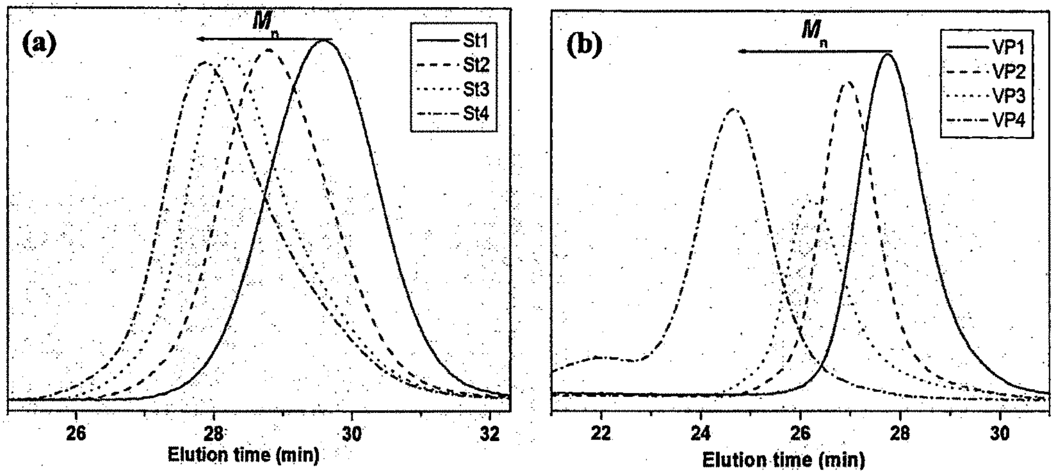


Figure 5.2. SEC chromatograms for (a) PSt (1) and (b) P2VP (2) showing the evolution of molecular weight with time.

5.4.2. Homopolymerization of 2VP (2)

The results for the homopolymerization of 2VP are summarized in Table 5.1 good agreement between the theoretical and experimental molecular weights is observed. Figure 5.2 (b) shows the overlay of the RI traces from the SEC analysis for the homopolymerization of P2VP (**2**) and clearly illustrates the increase in molecular weight with time which is qualitatively indicative of a controlled polymerization. However, a small shoulder appears {Figure 5.2 (b), VP4} at high molecular weight, probably corresponding to bimolecular termination by combination. The increase in molecular weight distribution with the long reaction time (molecular weight) is presumably the result of side reactions that become progressively more and more important.

5.4.3. Block cooligomerization of styrene with 2VP (3a and 3b)

Having confirmed that the homopolymerization of styrene and 2VP proceeds in a controlled manner with almost 100 % yield, and narrower molecular weight distribution, this technique was applied to the synthesis of diblock cooligomers of Styrene and 2VP. Table 5.2, summarizes the results of the block cooligomerization of styrene with 2VP in NMP. Styrene was polymerized for 15h, followed by the addition of 2VP to the polymerization mixture. In both the cases the evolution of the SEC chromatograms

{Figure 5.3, **(3a)** and **(3b)**} suggests complete disappearance of the PS macropromoter as the time of polymerization increases. All values of M_n are close to the theoretical values predicted for a "living" mechanism. The clear shift of the chromatograms in both cases to the higher molecular weight confirms the successful formation of the desired amphiphilic block cooligomers (**3a** and **3b**). The SEC elution profiles are unimodal suggesting no side reactions. Thus, diblock cooligomers of Styrene and 2VP of different P2VP well-controlled block lengths.

The number-average degrees of polymerization (DP_n) of the PS and P2VP were estimated from SEC as listed in Table 5.2. Two samples with different block lengths are denoted as poly(St_{20}-*b*-$2VP_{50}$) **(3a)** and Poly(St_{20}-*b*-$2VP_{20}$) **(3b)**. The molecular weight distribution is relatively narrow with M_w/M_n values ranging from 1.10 to 1.24 as estimated from SEC data. Figure 5.4 shows the ^1H NMR of the synthesized block copolymers, one can observe that the signals at 6.4-7.3 ppm corresponds to the aromatic protons of polystyrene and at 8.3 ppm the characteristics peaks of pyridine unit.

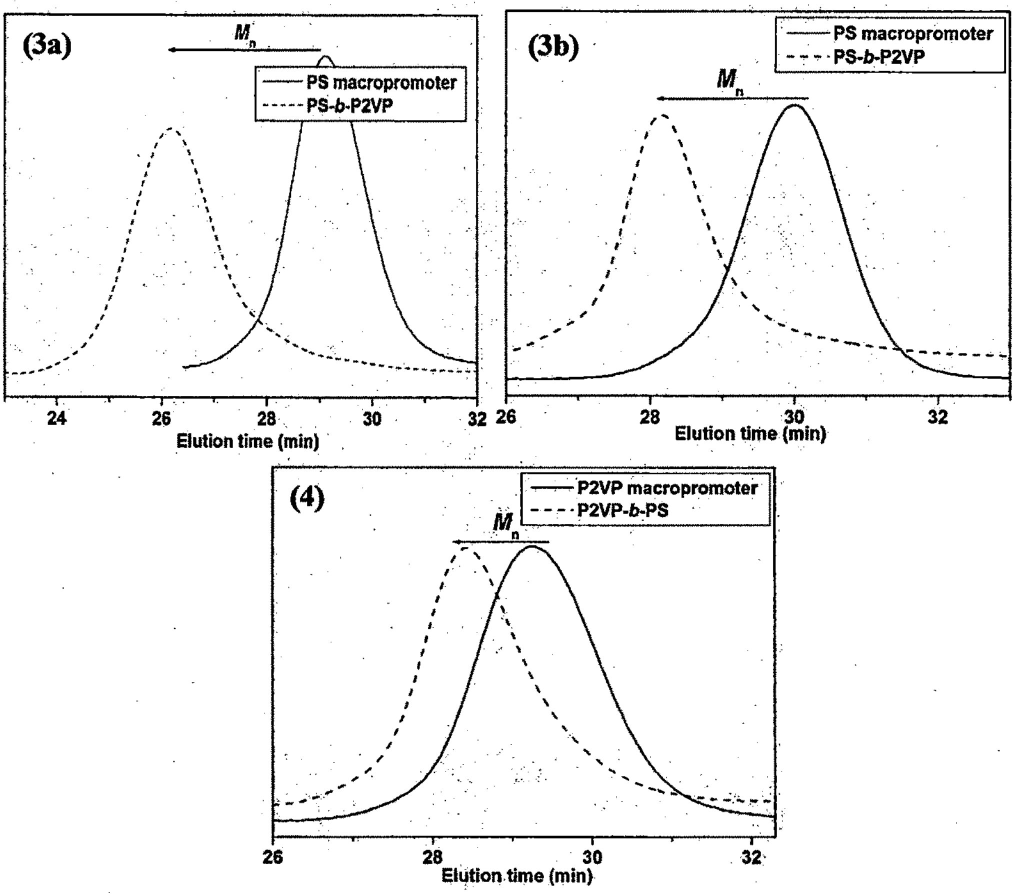


Figure 5.3. SEC chromatograms for PS, P2VP macropromoters and PS-b-P2VP, (3) P2VP-b-PS (4) block copolymers showing the evolution of molecular weight with time.

5.4.4. Block cooligomerization of 2VP with Styrene (4)

In order to check the versatility of the TERP block cooligomerization 2VP with Styrene was also performed. Table 5.2 summarizes the results the block cooligomerization in NMP. 2VP was polymerized first for 17 h followed by the addition of styrene to the polymerization mixture. The evolution of the SEC chromatograms {Figure 5.3, (4)} suggests the complete disappearance of the P2VP macropromoter as the time of polymerization increases. The values of M_n are close to the theoretical values predicted for a "living" mechanism. The clear shift of the chromatogram to the higher molecular weight confirms the successful formation of the desired amphiphilic block cooligomer (4). The SEC elution profiles are unimodal suggesting no side reactions. Thus, diblock copolymers of 2VP and styrene were obtained. The number-average degree of polymerization (DP_n) of the P2VP and PS were estimated from SEC as listed in Table 5.2, poly($2VP_{18}$-*b*-St_{12}) (**4**). The ^1H NMR analysis (Figure 5.4) of the synthesized block cooligomers (**3a**, **3b**, and **4**) in $CDCl_3$ showed the respective signals from 6.2 -7.4 ppm correspond to the aromatic protons of polystyrene and the signal at 8.3 ppm belongs to the protons from the pyridine moiety of the block cooligomer.

Table 5.2. Molecular Characteristics of Block copolymers of 2-vinylpyridine with styrene

Sample[z]	First Block		Block copolymers		
	M_n[a]	M_w/M_n[a]	$M_{n\ theo}$[b]	M_n[a]	M_w/M_n[a]
Poly(St_{20}-*b*-$2VP_{50}$) (**3a**)	2246	1.12	7503	7538	1.24
Poly(St_{20}-*b*-$2VP_{20}$) (**3b**)	2100	1.10	4202	4118	1.22
Poly($2VP_{18}$-*b*-St_{12}) (**4**)	1862	1.13	3111	3200	1.15

[z] See scheme 5.1. [a] M_n and M_w/M_n were measured by size-exclusion chromatography multiangle laser light scattering (Wyatt, mini-DAWN TREOS) and a refractive index detector (Shodex, RI-101). [b] M_n was calculated using the relation $M_{n\ theory} = M_{n,\ first\ block} + \{[M]_0/[AIBN]_0 \times \text{Molar mass of the monomer} \times 100\ \%\ \text{conversion}\}$.

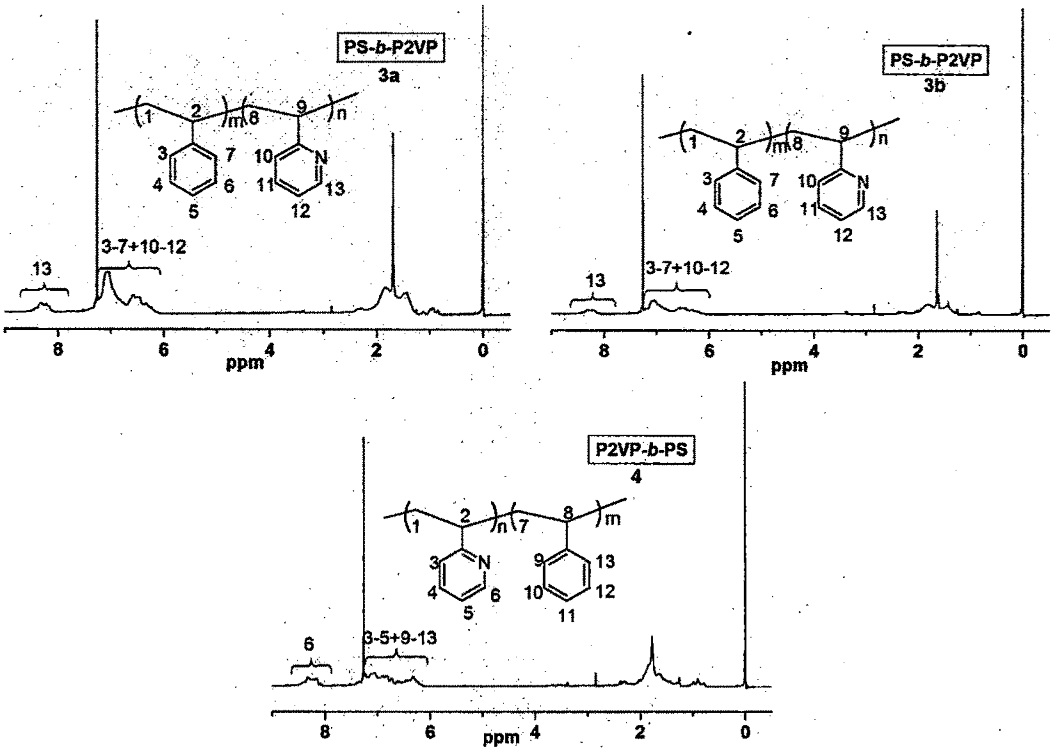


Figure 5.4. ***^{1}H NMR spectrum of PS-b-P2VP (3a and 3b) and P2VP-b-PS (4) in $CDCl_3$***

5.4.5. Quaternization of P2VP of block copolymers

Poly(2-vinylpyridine-*b*-styrene) (P2VP-*b*-PS, **4**) block cooligomer with P2VP mole fraction (f_{P2VP}) of 0.6, was used which was synthesized above. The molecular weight of **4** is 3111 and polydispersity index (M_w/M_n) is 1.15 as shown in Table 5.2. For nanoporous TiO2 membranes by using ionic interaction or hydrophilic interaction, the **4** was successfully quaternized by reaction with methyl iodide. Quaternization of pyridine nitrogen via solution nucleophilic substitution reaction increases the hydrophilic properties of PS-*b*-P2VP diblock copolymer.[50,51] So, the block copolymers of in which one block contains pyridine group or tertiary amine group can be amphiphillic block copolymers and block ionomers. The color of the obtained ionomers was yellow because of ionization of methyl iodide whereas the color of the parent P2VP-*b*-PS was white.

Quaternization was confirmed by Fourier-transform infrared (FT-IR) spectroscopy by observing the disappearance of the 1369 and 1303 cm^{-1} aromatic C-N stretching vibrations (Figure 5.2).[48]

The quaternized P2VP-*b*-PS has a hydrophobic polystyrene block and a hydrophilic pyridinium block. Therefore, it has a possibility of the formation of polymeric micelles in polar solvent or reverse micelles in non polar solvents. In case of reverse micelles, the styrene block is stretched in less polar solvent due to higher solubility. On the other hand, the pyridium block is aggregated in less polar solvent to reduce surface area due to less solubility.[52,53] The stretched portion of outside part is the "corona" and the aggregated portion of inner side part forms the "core".

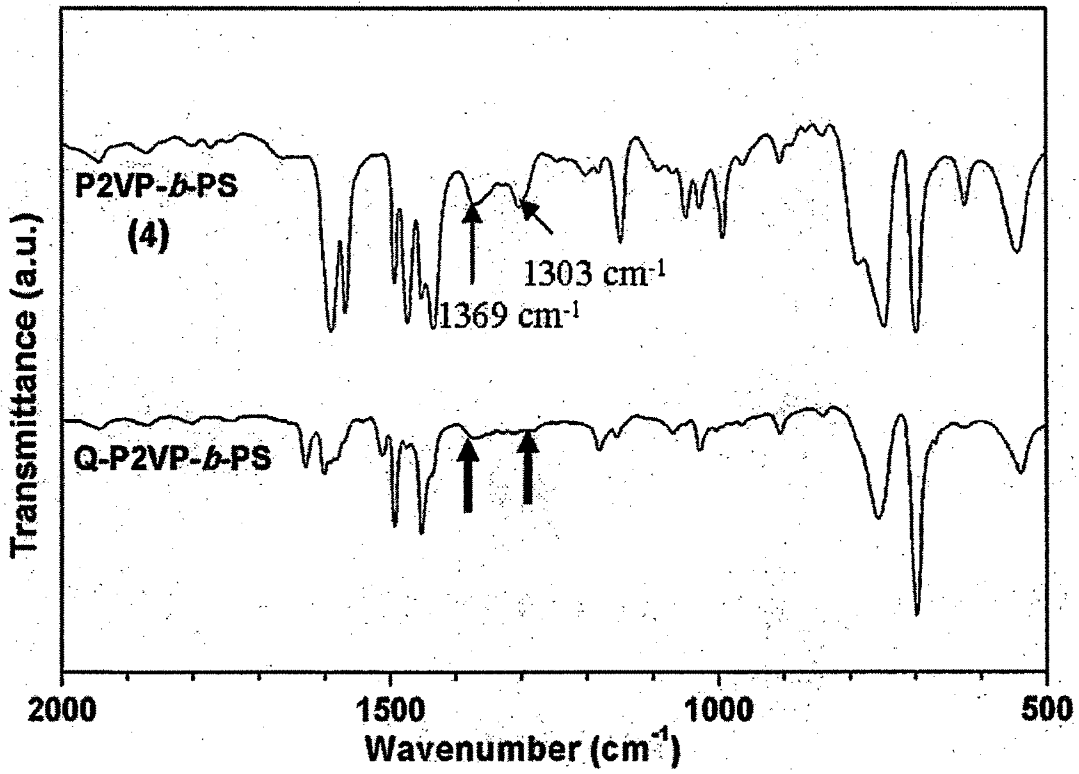


Figure 5.5. FT-IR spectra of the parent P2VP-b-PS and quaternized Q-P2VP-b-PS.

5.4.6. Formation of block cooligomer nanoparticle and TiO_2 Mesoporous membrane

The Q-P2VP-*b*-PS has a hydrophobic polystyrene block and a hydrophilic poly(2-vinylpyridine) block. It was possible to form polymeric micelles in selective solvent conditions. When the Q-P2VP-*b*-PS was dispersed in toluene, core-shell type polymeric nanoparticles were formed with a polystyrene shell.[50,51,54] The average diameter of the nanoparticles in toluene was observed 45 ± 5 nm as observed from TEM image of Figure 5.6 a and after incorporating the TiO_2 sol precursor (Figure 5.6 b), the TiO_2 grain size is 5 nm. One can clearly see that the TiO_2 nanoparticles are selectively bound to the core of the micellar nano structure.

There are several methods to prepare porous materials by removing organic nanoparticles in the bulk composites with titania precursors such as calcination, dissolution, and etching. To remove the Q-P2VP-*b*-PS nanoparticles, the composites layer was sintered at 600 °C for 4 hours which resulted in a nanoporous titania film.[55,56] Oxygen plasma etching was selected to remove Q-P2VP-*b*-PS nanoparticles. The Q-PS-*b*-P2VP composite film was exposed to oxygen plasma (100 W, 1.0×10^{-2} Torr) for 20 min. Figure 5.7 (c) and (d) show the successful synthesis of nanoporous titania layer prepared from a template of Q-P2VP-*b*-PS nanoparticles. It was confirmed that organic materials were completely removed by examining energy dispersive spectroscopy (EDS) profiles (Figure 5.8) which also confirms the synthesis of nanoporous TiO_2 membranes. The pore size of titania structure was approximately 50 nm.

This means that the polymer nanoparticle size and the pore size of titania structure matched. The nanoporous titania layer in Figure 5.7 was prepared from half the amount of precursor solution. Less than an optimum amount of titania precursor solution would result in the brittle and more porous nanoporous titania

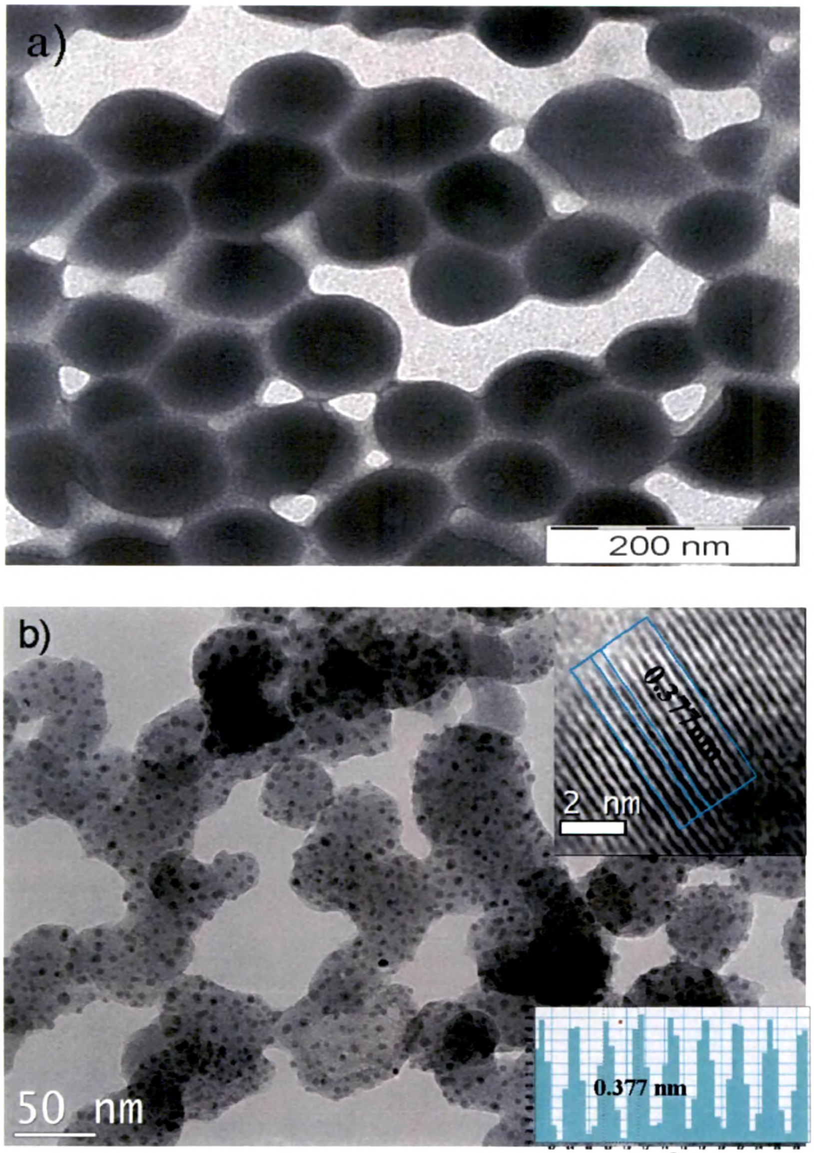


Figure 5.6. TEM images of Q-PS-b-P2VP nanoparticles: (a) without TiO_2 (b) with TiO_2, also accompanied by the corresponding HRTEM image and histogram showing the lattice spacing of 0.377 nm acquired from this sample which are matching with TiO_2 anatase structure[57]

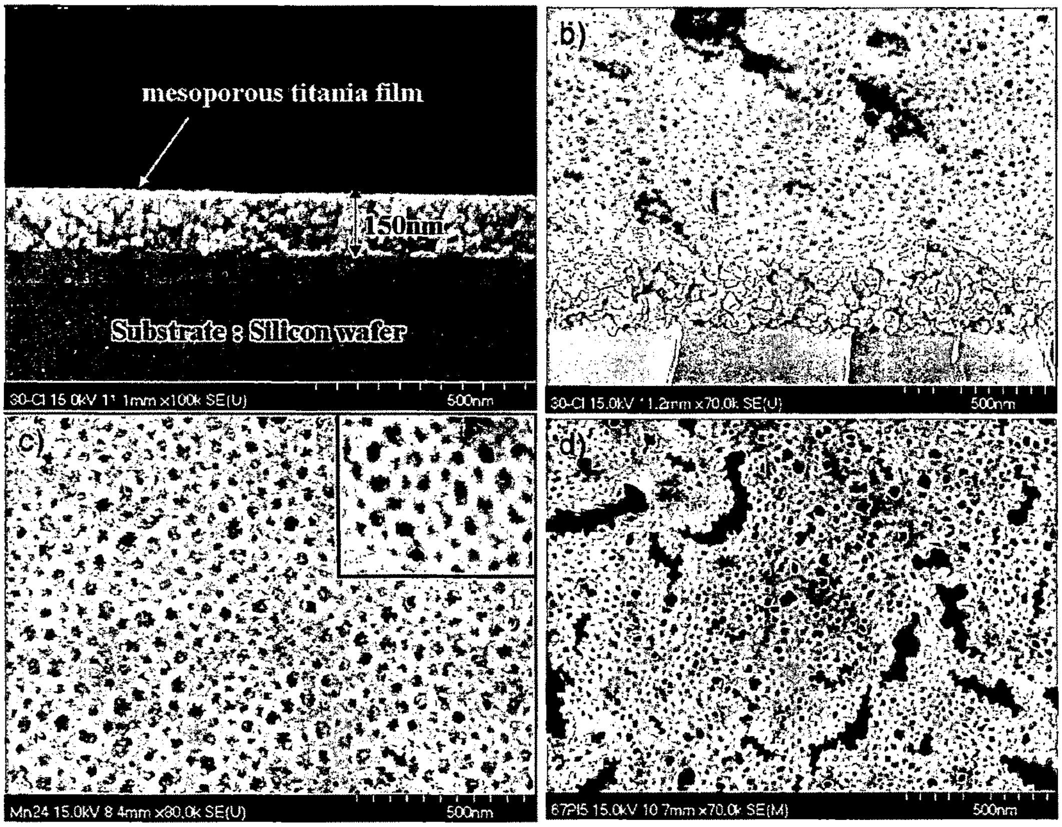
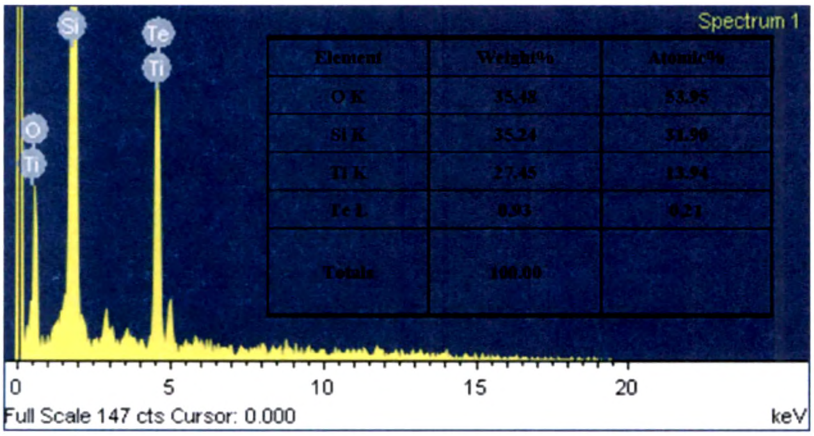


Figure 5.7. SEM images of nanoporous titania layer prepared by removing template of Q-PS-b-P2VP nanoparticles: (a) surface (b) 30° tilted cross-section nanoporous titania layers prepared by sintering at 600 °C for 4 hrs (c) surface view of nanoporous titania layers prepared by sintering at 600 °C for 4 hrs, and (d) Surface view of nanoporous titania layers prepared by oxygen plasma etching for 5 min.



Element	Weight%	Atomic%
O K	35.48	53.95
Si K	35.24	31.90
Ti K	27.45	13.94
Te L	0.93	0.21
Totals	100.00	

Figure. 5.8. Energy-dispersive X-Ray (EDX) spectra of as synthesized nanoporous titania layer prepared by removing template of Q-P2VP-b-PS nanoparticles after sintering.

5.5. Conclusion

The design and well-defined synthesis of low molecular weight polystyrene-*b*-poly (2-vinylpyridine) (PS-*b*-P2VP) and (P2VP-*b*-PS) an amphiphilic diblock cooligomer (which acts like a surfactants), for the first time via TERP has been successfully demonstrated in the present work. The good controllability, tolerance to functional groups and prominent robustness may be great advantages for this polymerization to serve as a useful synthetic tool for well-defined polymers. Thus, TERP provides a facile route for the synthesis of AB and BA diblock copolymers from Styrene and 2-vinylpyridine respectively.

The versatility and mild reaction conditions of this new method would be suitable for the mass production of structurally defined macromolecules. Mesoporous materials are generally prepared by using self-assembling anionic, cationic and non-ionic surfactant or block copolymers as templates, with inorganic precursors. Block copolymer have been increasingly used to organize mesostructured composite solids, because the architectures of the amphiphilic block copolymers can be rationally adjusted to control the interactions between the inorganic and organic species, self-assembly, and especially processibility more than possible with low molecular weight surfactants. The mesoporous composites with Titanium oxide and block copolymer were formed by using the electrostatic interaction. The block copolymer, PS-b-P2VPs with different MW and block ratio were polymerized to use them as the matrix of the mesoporous composite. For mesoporous composite by electrostatic interaction, P2VP block of P2VP-*b*-PS was quarternized by reaction with excess methyl iodide. The quarternized Q-P2VP-*b*-PS has a hydrophilic pyridium block and hydrophobic polystyrene block so it dissolved and formed micelle in toluene.

The TiO_2 was selectively embedded in P2VP domains. Mesoporous structure was formed by maximum sol solution concentration. To remove polymer, sintering and oxygen plasma etching were used. Thin films were prepared by spin-coating for application such as optical catalysts, chemical sensors, and dye-sensitized solar cell. The mesoporous size was about 50 nm. Our studies are now focused on extending the strategy to a wider range of vinyl polymerizations and investigating the applications of this approach.

5.6. References

(1) Frechet, J. M. J. *Science* **1994**, 263, 1710.

(2) Grayson, S. M.; Frechet, J. M. J. *Chem. Rev.*, **2001**, 12, 3819.

(3) Matyjaszewski, K.; Xia, J. *Chem. Rev.*, **2001**, 101, 2921.

(4) Kamigaito, M.; Ando, T.; Sawamoto, M. *Chem. Rev.*, **2001**, 101, 3689.

(5) *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: New York, 2002.

(6) Hawker, C. J.; Bosman, A. W.; Harth, E. *Chem. Rev.*, **2001**, 101, 3661.

(7) Matyjaszewski, K.; Davis, T. P. In *Handbook of Radical Polymerization*; Wiley Interscience: Hoboken, 2002

(8) Lutz, J.-F.; Pakula, T.; Matyjaszewski, K. In *Advances in Controlled/Living Radical Polymerization*; Matyjaszewski, K., Eds; ACS Symposium Series 854; American Chemical Society: Washington, DC, 2003, Chapter 19, pp 268.

(9) Matyjaszewski, K. In *Advances in Controlled/Living Radical Polymerization. Progress in ATRP, NMP, and RAFT.* ACS Symposium Series 768; American Chemical Society: Washington, DC, 2000.

(10) Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.*, **2002**, 124, 2874.

(11) Goto, A.; Kwak, Y.; Fukuda, T.; Yamago, S.; Iida, K.; Nakajima, M.; Yoshida, J. *J. Am. Chem. Soc.*, **2003**, 125, 8720.

(12) Kwak, Y.; Goto, A.; Fukuda, T.; Kobayashi, Y.; Yamago, S. *Macromolecules*, **2006**, 39, 4671.

(13) Chiefari, J.; Rizzardo, E. In *Handbook of Radical Polymerization*; Matyjaszewski, K.; Davis, T. P., Eds.; Wiley Interscience: Hoboken, 2002, Chapter 12, 621.

(14) Lee, J. M.; Kim, O. H.; Shim, S. E.; Lee, B. H.; Choe, S. *Macromol. Res.*, **2005**, 13, 236.

(15) Perrier, S.; Takolpuckdee, P. *J. Polym. Sci., Part A: Polym. Chem.*,**2005**, 43, 5347.

(16) Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.*, **2002**, 124, 2874.

(17) Yamago, S.; Iida, K.; Yoshida, J. *J. Am. Chem. Soc.*, **2002**, 124, 13666.

(18) Yamago, S. *J. Polym. Sci., Part A: Polym. Chem.*, **2006**, 44, 1.

(19) Yusa, S.; Yamago, S.; Sugahara, M.; Morikawa, S.; Yamamoto, T.; Morishima, Y. *Macromolecules,* **2007**, 40, 5907.

(20) Creutz, S.; Teyssie, P.; Jerome, R. *Macromolecules,* **1997**, 30, 1.

(21) Quirk, R. P.; Corona-Galvan, S. *Macromolecules,* **2001**, 34, 1192.

(22) Gohy, J. F.; Antoun, S.; Jerome, R. *Macromolecules,* **2001**, 34, 7435.

(23) Lee, J.; Hogen-Esch, T. E. *Macromolecules,***2001**, 34, 2805.

(24) Rahman, M. S.; Samal, S.; Lee, J. S. *Macromolecules,* **2007**, 40, 9279.

(25) Chen, Z.; Cai, J.; Jiang, X.; Yang, C. *J. Appl. Polym. Sci.*, **2002**, 86, 2687.

(26) Lokaj, J.; Holler, P. *J. Appl. Polym. Sci.* **2001**, 80, 2024.

(27) Ding, X. Z.; Fischer, A.; Brembilla, A.; Lochon, P. *J. Polym. Sci., Polym. Chem.*, **2000**, 38, 3067.

(28) Fischer, A.; Brembilla, A.; Lochon, P. *Macromolecules,* **1999**, 32, 6069.

(29) Chalari, I.; Pispas, S.; Hadjichristidis, N. *J. Polym. Sci., Part A: Polym. Chem.*, **2001**, 39, 2889.

(30) Convertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; Mccormick, C. L. *Macromolecules,* **2003**, 36, 4679.

(31) Matyjaszewski, K; Gaynor, S. G.; Qui, J.; Beers, K.; Coca, S.; Davis, K; Muhlebach, A; Xia, J.; Zhang, X. In *Associative Polymers in Aqueous Media*: Glass, J. E., Ed.; American Chemical Society: Washington, DC, 2000; 52.

(32) Ramakrishnan, A.; Dhamodharan, R. *J. Macromol. Sci., Pure Appl. Chem.*, **2000**, A37, 621.

(33) Xia, J.; Zhang, X.; Matyjaszewski, K. *Macromolecule,s* **1999**, 32, 3531.

(34) Huang, C. F.; Kuo, S. W.; Chen, J. K.; Chang, F. C. *J Polym Res,* **2005**, 12, 449.

(35) Yu, Y. Y.; Chien, W. C.; Chen, S. T. *Poly Int,* **2008**, 57, 1369.

(36) Dasgupta, A.; Sivaram, S. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.,* **1997**, C37, 1.

(37) Hashimoto, T.; Harada, M.; Sakamoto, N. *Macromolecules,* **1999**, 32, 6867.

(38) Zhao, H.; Douglas, E. P.; Harrison, B. S.; Schanze, K. S. *Langmuir,* **2001**, 17, 8428.

(39) Cho, J. H.; Cho, G.; Lee, J. S. *Adv. Mater.,* **2004**, 16, 1814.

(40) Cho, Y. S.; Ihn, C. S.; Lee, H. K.; Lee, J. S. *Macromol. Rapid Commun.,* **2001**, 22, 1249.

(41) Shin, Y. D.; Han, S.-H.; Samal, S.; Lee, J. S. *J. Polym. Sci. Part A: Polym. Chem.,* **2005**, 43, 607.

(42) Kang, N. G.; Changez, M.; Lee, J. S. *Macromolecules* **2007**, 40, 8553.

(43) Kang, N. G.; Kang, B. G.; Koh, H. D.; Changez, M.; Lee, J. S. *React. Funct. Polym.,* **2009**, 69, 470.

(44) Hagfelf, A.; Gratzel, M. *Chem. Rev.*, **1995**, 95, 49.

(45) Moriguchi, I.; Maeda, H.; Teroka, Y.; Kagawa, S. *Chem. Mater,.* **1997**, 9, 1050.

(46) Hoyer, P.; Masuda, H. J. *Mater. Sci. Lett.,* **1996**, 16, 1228.

(47) Matsushita, S. I.; Miwa, T.; Tryk, D. A.; Fujishima, A. *Langmuir,* **1998**, 15, 6441.

(48) Zhu, J.; Eisenberg, A.; Lennox, R. B. *Macromolecules,* **1992**, *25*, 6547.

(49) P. Joachim .Spatz, S. MÖssmer, C. Hartmann, M.Moller, *Langmuir,* **2000**, 16, 407.

(50) Cho, Y. H.; Cho, G.; Lee, J. S. *Adv. Mater.* **2004**, 17, 1815.

(51) Goh, H. D.; Kang, N. G; Lee, J. S. *Langmuir,* **2007**, 23, 12817.

(52) Desjardins, A.; Eisenberg, A. *Macromolecules,* **1991**, 24, 5779.

(53) Gao, Z.; Desjardins, A.; Eisenberg. A. *Macromolecules,* **1992**, 25, 1300.

(54) Cho, Y.-H.; Yang, J.-E.; Lee, J.-S. *Mater. Sci. Eng., C* **2004**, 24, 293.

(55) Xia, Y.; Gates, B.; Yin, Y.; Lu, Y. *Adv. Mater.,* **2000**, 12, 693.

(56) Gates, B.; Yin, Y.; Xia, Y. *Chem. Mater.*, **1999**, 11, 2827.

(57) Carol, L. D.; Carlino,E.; Caputo, G.; Cozzoli, P. D.; Giannini, C. *Nature Nanotech.*, **2010**, 5, 360.