ISSN : 0974 - 7486 Volume 9 Issue 9

Trade Science Inc.

Materials Science

An Indian Journal

Full Paper

MSAIJ, 9(9), 2013 [352-358]

Plasma enhanced synthesis of stimuli responsive membranes

K.Smolińska, M.Bryjak*

Department of Polymer and Carbon Materials, University of Technology, Wroclaw, (POLAND)

ABSTRACT

Porous polycarbonate and polypropylene membranes were grafted with stimuli responsive polymers that formed brush-like structure. The grafting from mode was applied. Efficiency of modification was compared for two kinds of plasma - dielectric barrier discharge plasma and microwave plasma. The following thermo- and pH-sensitive polymers were used poly(N-izopropyloakryamide), poly(propylene oxide-co-ethylene oxide) and poly(acrylic acid). It was found that grafted membranes showed different water permeability when temperature and pH changed and their responses to external stimuli were related to the kind of used membrane mostly. It was noted that the use of both plasmas resulted in preparation of membranes with similar grafting yield. Taking into account the simplicity of equipment used, the dielectric barrier discharge plasma has been suggested for preparation of such nanostructured membranes.

KEYWORDS

Polymer brushes;
Smart polymers;
Membrane valves.

INTRODUCTION

Membranes with environmentally-sensitive polymers have become intensively studied in last decades. They are prepared by two methods: i) blending of responsive polymer with standard polymer and processing the blend to prepare membranes with embedded responsive elements or ii) attaching responsive polymer to porous substrate[1]. The last method can be conducted by direct grafting of polymer brushes to pore walls or by *in situ* polymerization of stimuli responsive polymers within pores. The works of Mika et al.[2-6] showed huge application potential of the attached stimuli sensitive polymers. It was shown that phase transition of gel fixed into pores have affected the either viscous flow or membranes selectivity[5,6]. The unique character of such membranes were reflected by calling them McMaster membranes. However, the method for their synthesis was not simple and fast enough. The McMaster membranes were prepared by photoradical polymerization of monomers into pores[7]. The syntheses routes need the use photoinitiator and conduct polymerization at elevated temperature. It seems that plasma induced introduction of radicals to pore walls should make the preparation step simple and fast.

Lately, plasma modification becomes very attractive method for alteration of surface properties. There are two features that justify that interest: production of small amounts of by-products and extremely short time of modification. The presented study deals with comparison of modification efficiency for two plasmas: dielectric barrier discharge, DBD, and microwave, MW, in preparation of stimuli responsive membrane. DBD plasma belongs to the group of processes that are run under the normal pressure. Electrodes biased by a low-frequency current with high voltage are arranged very close each to the other. Ionized gas changes the surface chemistry when a sample is attached to one electrode. In the case of MW plasma, gas activation occurs at a remote place of the system and activated molecules bombard sample surface. The minus of MW plasma is a need to run it at low pressure in a plasma chamber[8-12].

Generally, there are two approaches for surface grafting: i) to induce radicals on the surface and polymerize monomers (grafting from method, and ii) to attach polymer chains to surface by plasma action[13]. The effectiveness of the last method in grafting stimuli responsive polymers is evaluated in this paper.

There are some macromolecules that are able to change their properties with respect to temperature, pH, ionic strength, light, etc. Grafting such polymers onto porous surface results in creation of stimuli responsive structures that can control membrane permeability with response to different environmental conditions. Poly(*N*-isopropylacrylamide), PNIPAM, is one of the well recognized thermosensitive polymer. In water, it exhibits lower critical solution temperature at 32°C[14-19]. Copolymer of ethylene oxide and propylene oxide, poly(EO-co-PO), has similar properties at more elevated temperature (40-50^{0}C)[20,21]. Poly(acrylic acid), PAA, changes its properties when pH varies. Its pK=4.5 shows that chains collapse at acidic conditions[22-25].

The paper is aimed to show the best conditions for preparation of stimuli responsive membranes by plasma treatment. To do it two microporous membranes, two plasma activation methods and three kinds of stimuli responsive polymers were used to obtain smart membranes.

EXPERIMENTAL PART

Materials and equipment

Porous polypropylene membrane, PP, - Celgard 2500 of thickness 25.4 μm, average pore - 0.20 μm and porosity of 45% was used as polyolefin substrate representative.

Polycarbonate membranes, PC, - Nucleopore of pore size of 0.1, 0.2 or 0.4 μm was used as polyaromatic substrates representative.

N-izopropylacrylamide, NIPAM, (Sigma Aldrich) recrystallized from n-hexane. Poly(acrylic acid) (Mw = 50,000 Da) delivered by Polysciences.

Copolymer poly(propylene oxide-co-ethylene oxide) 30P160, (Mw=10,100 Da, average ratio of moles propylene oxide to ethylene oxide as 30:160) was gifted by CCP Rokita, Poland.

Poly(N-isopropylacrylamide), PNIPAM, was obtained by radical polymerization of NIPAM monomer, 7.5%, in aqueous solution with potassium persulfate, 0.52%, as initiator. Polymerization was carried at 80^{0}C for 5 hrs. Filtered product was dried in vacuum at room temperature. The yield of polymerization – 74%, and viscosity average molecular weight – 1,200 kDa.

Plasma reactors

Microwave plasma system, of 2.45 GHz frequency, with adjustable power source (ERTEC, Poland) and dielectric barrier plasma, DBD, system (Dora Power System, Poland) with adjustable current, voltage and pulse frequency were used throughout this study. Argon served as gas in both systems.

The following plasma parameters were chosen for membrane activation:

(a) MW plasma

- for both kind of membranes: 170 W plasma power, pressure in the plasma chamber 0.5 Torr, distance from plasma edge to sample surface – 7 cm, modification time - 5 min.

(b) DBD plasma

- for PC membranes: 15kV, 5 mA, argon flow 60 l/h, pulse time 0.5 ms, pulse cycle 10ms, modification time 1 min, distance between electrodes – 0.5 mm.
- for PP membranes: 20kV, 5 mA argon flow 60 l/h, pulse time 0.5 ms, pulse cycle 10ms, modification time 1 min, distance between electrodes – 0.5 mm.

Determination of radicals concentration

Peroxide concentration on modified membranes was determined by 2,2-diphenyl-1-picrylhydrazyl hydrate, DPPH, method[26]. The membranes, blank and plasma modified, were immersed in 0.1 M solution of

DPPH in benzene and exposed to UV lights (2 kW) for 5 min. The solution absorbance was determined before and after UV illumination. Radicals concentration was calculated from the following relationship

$A = C\,L\,\varepsilon$

where A – absorbance at 520 nm, L –optical path thickness and $\varepsilon = 1{,}18 \times 10^4$ l/mol cm

Grafting protocols

(a) Grafting after DBD or MW plasma activation

After the plasma activation the membranes were exposed to air for 10 min. Grafting of stimuli responsive polymers was carried out by immersing membranes in aqueous solution of suitable polymer and illuminating them with UV light, 2 kW lamp for 3 min. Grafting parameters are shown in TABLE 1. After grafting the membranes were washed with large volume of water to remove unbound polymer.

TABLE 1 : Grafting parameters when membranes were activated in DBD plasma.

Membrane	Polymer		
	PNIPAM	P(PO-co-EO)	PAA
Polycarbonate	Solution concentration, wt%		
	1, 2 or 3	10	25
	Temperature of grafting, °C		
	60	60	60
	Time for grafting, min		
	240	240	240
Polypropylene	Solution concentration, wt%		
	7.5	10	25
	Temperature of grafting, °C		
	60	60	60
	Time for grafting, min		
	240	240	240

Membrane characterization

(a) Grafting degree

Grafting degree was calculated gravimetrically and expressed in, g/cm², according to the following formulae:

$GY = (W_1 - W_2)/S$

where W_1 and W_2 are weights of membrane after and before grafting, and S membrane area.

(b) ATR-FTIR spectroscopy

Wide scans of grafted membranes were obtained on Perkin-Elmer System 2000 spectrophotometer equipped with ATR device (Ge, 45°). 250 scans were collected with 4cm^{-1} resolution.

(c) Filtration process

The response of membranes to various temperature and at different pH was tested in Amicon 8200 filtration cell at 20 and 45°C, for PNIPAM modified membranes and at pH 3.5 and 10.5, for PAA membranes. For all measurements 0.05 MPa overpressure was applied. Before filtration, membranes were hydrofilized in 50% water:ethanol solution for 30 min.

RESULTS

When one uses two different plasmas for surface activation one should expect that they create different amount of surface peroxides. To check this hypothesis the peroxide concentration generated by DBD and MW plasmas on PC and PP membranes was determined. The results are listed in TABLE 2.

TABLE 2 : Amount of formed peroxides on modified membranes.

Plasma	Membrane	Peroxide concentration[1] [nmol/cm^2]
DBD	PP	3.45
	PC*	1.24
MW	PP	4.21
	PC*	0.98

***polycarbonate membrane with pores of 0.2 μm was taken; #accuracy of peroxide determination less than 20%, the data corrected for blank samples**

The inspection of obtained data allows rejection of the hypothesis: both evaluated plasmas showed the same efficiency in creation of peroxides functionalities on the membrane surfaces. Hence, both of them could be used for grafting of stimuli responsive polymers. However, a different amount of radicals was created on the membranes: polypropylene membrane had 4-times more peroxides than polycarbonate membrane.

Polycarbonate membranes

When DBD plasma activated membranes were exposed to the air some amount of peroxide functionalities were formed on the surface. After immersing these membranes in a polymer solution and exposing it to UV light the chains should be attached to membrane[1,4]. The properties of PC membranes grafted with PNIPAM, 30P160, and PAA are listed in TABLE 3.

TABLE 3 : Characteristics of PC membrane grafted with PNIPAM, 30P160, and PAA. Dielectric barrier plasma case.

Grafted polymer	Membrane pore size [μm]	Concentration of polymer [%]	Grafting degree [mg/cm^2]	Permeate flux [dm^3/m^{2}h] Before modification	Permeate flux [dm^3/m^{2}h] After modification	
				$T=20^{0}C$	$T=20^{0}C$	$T=45^{0}C$
PNIPAM	0.1	1	0.0061	32	10	99
		2	0.0021	33	4	87
		3	0.0040	38	5	96
	0.2	1	0.0055	52	0	27
		2	0.0060	54	0	90
		3	0.0087	56	0	77
	0.4	1	0.0081	236	0	225
		2	0.0070	235	0	189
		3	0.0100	210	0	223
30P160	0.1	10	0.0072	30	59	65
	0.2		0.0064	45	41	46
	0.4		0.0066	235	187	201
				pH= 3.5	pH= 3.5	pH=10.5
PAA	0.1	25	0.0021	35	17	0
	0.2		0.0040	55	37	0
	0.4		0.0055	236	160	0

PC membranes grafted with PNIPAM behaved as thermo-sensitive membranes: they did not allow water to pass at room temperature but they were well permeable at 45°C. What is more, this effect was detected for membranes obtained by grafting of PNIPAM from either low or high concentrated solutions. In the case of 30P160 copolymer, it was no observed any relation between water flux and temperature. That confirmed low sensitivity of poly(propylene oxide-co-ethylene oxide) copolymer to temperature changes. Grafting of PAA resulted in getting pH-sensitive membranes. The content of grafted poly(acrylic acid) chains was large enough to plug pores when the chains were swollen. When pH dropped below pK of carboxylic groups, shrunken chains opened pores and membranes became permeable.

Similar relationship was noted for PC membranes treated in microwave plasma (TABLE 4). Generally speaking, MW plasma caused grafting on the same extend as DBD plasma and obtained membranes showed similar properties: PNIPAM and PAA were sensitive to temperature and pH change respectively, while 30P160 grafted membranes did not show any significant flux alteration at different temperatures.

ATR-FTIR spectroscopy was used to check chemical composition of the modified membranes. Figure 1 presents IR spectra of neat PC membrane (a) and membrane grafted with PNIPAM (b, c). The peaks at 1540 cm^{-1} and 1650 cm^{-1}, attributed to C=O i N-H groups, indicate presence of PNIPAM. More intensive absorption bands appeared for MW plasma and confirmed higher degree of grafting for it. However, one cannot forget that higher concentration of PNIPAM was used to the synthesis. In the case of 30P160 copolymer, the spectra (see Figure 2) show peaks characteristic for C-O groups in the 1050-1200 cm^{-1} region. It means that this copolymer was grafted to polycarbonate support also. For DBD and MW plasmas, polycarbonate membranes grafted with PAA showed peaks at 1558 and 1457 cm^{-1} attributed to carboxylates (see Figure 3). Presence of peak at 1715 cm^{-1}, related to C=O structure, confirms presence of poly(acrylic acid) on the membrane surface. There were no differences between IR spectra for membranes prepared by means of both plasmas.

TABLE 4 : Characteristics of PC membrane grafted with PNIPAM, 30P160, and PAA. Microwave plasma case.

Grafted polymer	Membrane pore size [μm]	Concentration of polymer [%]	Grafting degree [mg/cm^2]	Permeation flux [dm^3/m^{2}h] Before modification	Permeation flux [dm^3/m^{2}h] After modification	
				$T=20^{0}C$	$T=20^{0}C$	$T=45^{0}C$
PNIPAM	0.1	7.5	0.0024	38	25	248
	0.2		0.0026	52	0	240
	0.4		0.0027	236	0	189
30P160	0.1	10	0.0070	62	25	52
	0.2		0.0071	46	10	25
	0.4		0.0069	250	37	60
				pH=3.5	pH=3.5	pH=10.5
PAA	0.1	25	0.0023	32*	20	0*
	0.2		0.0021	50	60	0
	0.4		0.0025	191	106	15

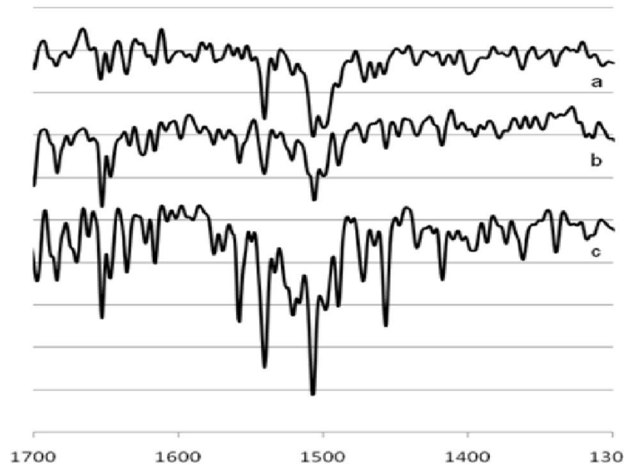

Figure 1 : FTIR spectra a) no modified membrane PC, b) membrane with PNIPAM modified by DBD plasma, c) membrane with PNIPAM modified by MW plasma.

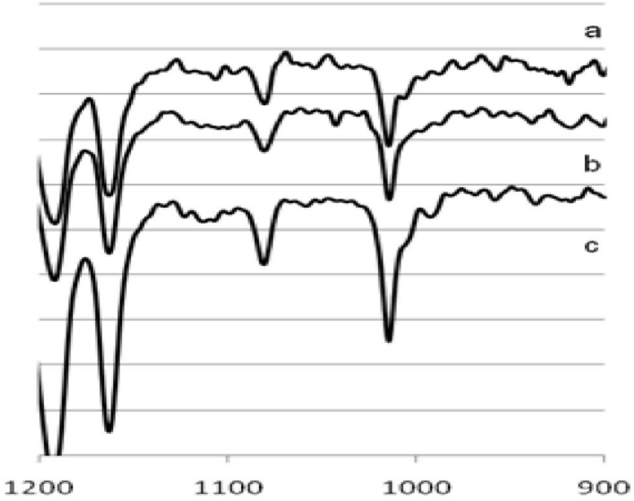

Figure 2 : FTIR spectra a) no modified membrane PC, b) membrane with 30P160 modified by DBD plasma, c) membrane with 30P160 modified by MW plasma.

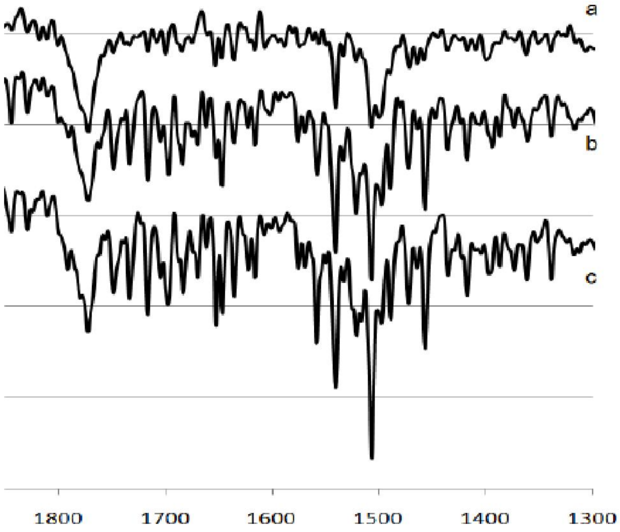

Figure 3 : FTIR spectra a) no modified membrane PC, b) membrane with PAA modified by DBD plasma, c) membrane with PAA modified by MW plasma.

Polypropylene membranes

In preparation of responsive membranes by grafting PNIPAM or PAA to plasma activated PC membranes, DBD and MW plasmas appeared to be equivalent: the obtained membranes showed similar character. Hence, taking into account simplicity of the use of DBD plasma this method was applied for polypropylene membranes. The procedure of polymer grafting was the same as in the case of PC membranes. Permeability of prepared membranes is shown in Figures 4 and 5.

As one predicts, PNIPAM membranes showed excellent thermosensitive behavior even when small amounts of poly(N-isopropylacrylaminde) were grafted to. The same phenomenon was observed for PAA membranes: with low grafting yield they behaved as valves and changed permeability with alteration of feed pH. However, for large grafting yield all pores were blocked and water was not able to pass through membrane. Hence, selection of materials for the use as the stimuli responsive valve is mostly related to the grafting yield of polymer brushes.

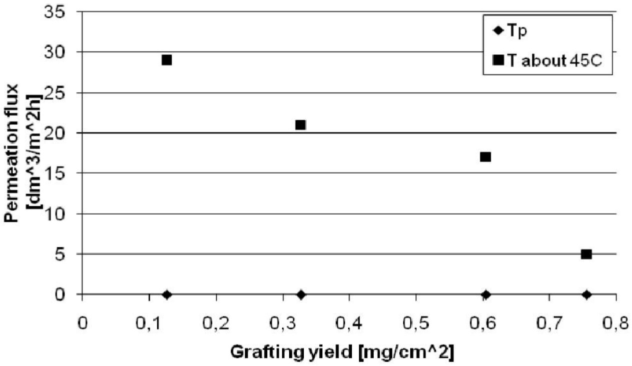

Figure 4 : Membrane permeation as the function of grafting yield. PP membrane with PNIPAM.

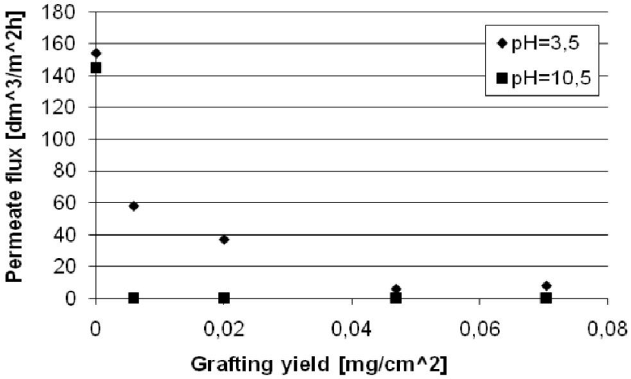

Figure 5 : Membrane permeation as the function of grafting yield. PP membrane with PAA.

ATR-FTIR spectroscopy was used to characterize chemical composition of modified PP. The obtained spectra are shown in Figures 6 and 7.

Figure 6 illustrates IR spectra of neat PP membrane (a) and the same membrane with grafted PNIPAM (b). As was mentioned for PC membranes, the peaks at 1540 cm^{-1} and 1650 cm^{-1} were attributed to C=O and N-H groups absorption. Hence, they gave an evidence that PNIPAM was located on the surface of PP membrane. In the case of membranes grafted with PAA chains (Figure 7) peaks at 1457, 1560 and 1715 cm^{-1} are characteristic for carboxylic functionality. These peaks appeared in spectrum of PP membrane grafted with PAA and proved presence of poly(acrylic acid) on the membrane surface.

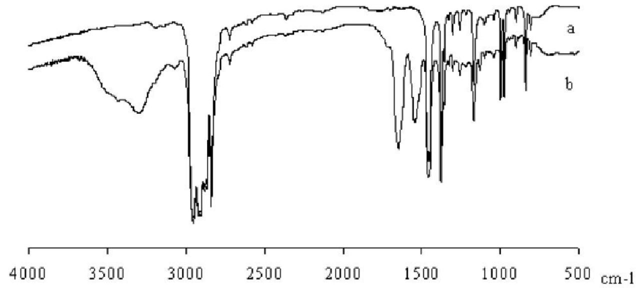

Figure 6 : FTIR spectra a) not modified membrane PP, b) membrane with PNIPAM modified by DBD plasma.

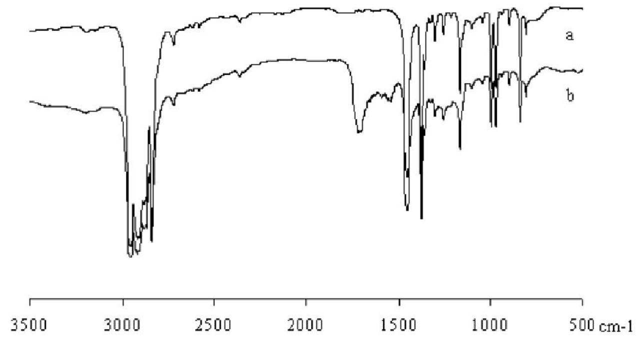

Figure 7 : FTIR spectra a) not modified membrane PP, b) membrane with PAA modified by DBD plasma.

CONCLUSIONS

In the synthesis of stimuli responsive membranes, the use of both plasma methods resulted in manufacturing similar products. Grafting of PNIPAM to PC or PP microfilters offered thermosensitive membrane while grafting of PAA resulted in pH sensitive membranes. It seemed that even the small grafting amount of polymer brushes to both substrates resulted in preparation of membranes that could response to the change of pH or temperature. Taking into account that PC microfilters had narrower pore size distribution than PP membranes had and that PP substrate was able to keep more radicals after activation, Celgard 2500 micro-filters seemed to be more efficient in preparation of stimuli responsive membrane valves. Even the largest pores could be blocked by grafted chains and the whole system does not lose its ability to response to external stimuli. Activation in DBD plasma was as much effective as activation in MW plasma but simplicity in its operation raised dielectric barrier discharge plasma device to the top of systems for plasma modification.

ACKNOWLEDGEMENT

The authors appreciate support of NanoMat project 'The use of nanotechnology in modern materials' financed in frame of POIG 01.01.02-02-002/08

REFERENCES

[1] D.R.Latulippe, A.M.Mika, R.F.Childs, R.Ghosh, C.D.M.Carlos Filipe; J.Membr.Sci., **342**, 227 **(2009)**.

[2] A.M.Mika, R.F.E.F.Childs, M.West, J.N.A.Lott; J.Membr.Sci., **136**, 221 **(1997)**.

[3] A.M.Mika, R.F.E.F.Childs, J.M.Dickson; J.Membr.Sci., **153**, 45 **(1999)**.

[4] A.M.Mika, R.F.E.F.Childs, J.M.Dickson; J.Membr.Sci., **206**, 19 **(2002)**.

[5] A.M.Mika, R.F.Childs, J.M.Dickson; Desalination, **121**, 149 **(1999)**.

[6] A.M.Mika, R.F.Childs, J.M.Dickson, M.E.McCarry, D.R.Gagon; J.Membr.Sci., **108**, 37 **(1995)**.

[7] J.Garcia-Aleman, J.Dickson, A.Mika; J.Membr.Sci., **240**, 237 **(2004)**.

[8] I.Gancarz, M.Bryjak, J.Kunicki, A.Ciszewski; J.Appl.Polym.Sci., **116**, 868 **(2009)**.

[9] X.Wang, GM.McCord; J.Appl.Polym.Sci., **104**, 3614 **(2007)**.

[10] I.Gancarz, J.Kunicki, A.Ciszewski; Chemickie Listy, **102**, 1467 **(2008)**.

[11] A.Ciszewski, I.Gancarz, J.Kunicki, M.Bryjak; Surface & Coating Technology, **201**, 3676 **(2006)**.

[12] M.Bryjak, I.Gancarz; Membrane prepared via plasma modification, in membranes for membrane reactors, A.Basile, F.Gallucci (Eds); Willey, 475 **(2011)**.

[13] M.Bryjak, I.Gancarz, K.Smolinska; Adv.Colloid Interface Sci., **161**, 2 **(2010)**.

[14] T.D.Nguyen, K.C.F.Leung, M.Liong, Y.Liu, J.F.Stoddart, J.I.Zink; Adv.Funct.Mater., **17**, 2101 **(2007)**.

[15] S.J.Lue, J.J.Hsu, Ch.H.Chen, B.Ch.Chen; J.Membrane Sci., **301**, 142 **(2007)**.

[16] S.J.Lue, J.J.Hsu, T.Ch.Wei; J.Membrane Sci., **321**, 146 **(2008)**.

[17] I.Csetneki, G.Filipcsei, M.Zrinyi; Macromolecules, **39**, 1939 **(2006)**.

[18] W.Lequieu, N.I.Shtanko, F.E.Du Prez; J.Membrane

Sci., **256**, 64 **(2005)**.

[19] M.R.Palomares; J.Chromatogr B, **807**, 3 **(2004)**.

[20] J.Persson, H.-OJohansson, F.Tjerlend; J.Chromatogr A, **864**, 31 **(1999)**.

[21] M.Pereira, Y.-TWu, A.Venancio; Teixeira J.Biochem. Eng.J., **15**, 131 **(2003)**.

[22] B.D.Johnson, D.J.Beebe, W.C.Crone; Mater.Sci. Eng.C, **24**, 575 **(2004)**.

[23] Q.Yu, J.M.Bauer, J.S.Moore, D.J.Beebe; Appl. Phys.Lett., **78**, 2589 **(2001)**.

[24] D.J.Beebe, J.Moore, J.Bauer, Q.Yu, R.H.Liu; C.Devados; Nature, **404**, 588 **(2000)**.

[25] C.Ruan, K.Zeng, C.A.Grimes; Anal.Chim.Acta, **497**, 123 **(2003)**.

[26] M.Ulbricht, G.Belfort; J.Membr.Sci., **111**, 193 **(1966)**.