

## Preparation of Enduringly Antifouling PVDF Membrane with Compatible Zwitterionic Copolymer via Thermally Induced Phase Separation

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**ABSTRACT:** The compatible zwitterionic copolymers of poly(methyl methacrylate [3-(methacryloylamino)propyl]dimethyl(3-sulfopropyl)ammonium-hydroxide) p(MMA-MPDSAHA) with different MPDSAHA ratio are synthesized by free radical polymerization. A series of copolymers are obtained successfully with narrow molecular weight dispersion. The MPDSAHA branch ratio varies from 5% to 20%. It is initially applied to fabricate enduringly antifouling poly(vinylidene fluoride) (PVDF) membrane through a simple approach of blending by thermally induced phase separation (TIPS). The influence of zwitterionic copolymer on membrane morphology is studied by scanning electron microscopy. It was proven effective to improve the hydrophilic property of PVDF membrane as the water contact angles dramatically decreased from 80° to 40°, leading to a significant enhancement of antifouling ability. The absorbed bull serum albumin (BSA) content on modified membranes has cut almost 50%. The residual content of p(MMA-MPDSAHA) in membrane is over 40% and able to reach 80% even at vigorous rinsing by controlling copolymer structure. It guarantees the modified membrane has vested enduringly antifouling ability. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41362.

**KEYWORDS:** blends; copolymers; membranes

Received 16 April 2014; accepted 1 August 2014

DOI: 10.1002/app.41362

### INTRODUCTION

Nowadays, zwitterionic polymer containing both anionic and cationic groups on a molecular chain has received extensive attention of researchers as it exhibits special interaction effects such as pH responsive, heavy metal-ion adsorption, and self-assembly behavior. The properties of the zwitterionic polymer are mainly determined by their structure and chemical composition. Natural zwitterionic polymers such as protein and nucleic acid which contain amino group and carboxyl group are important functional materials in organism. Synthesized zwitterionic polymers possess control-designed structure and flexible properties for several anion groups such as carboxyl group, sulfo group, and phosphate group can be selected to combine with amino derivatives as anionic group and different chain structure can be designed in reaction. It has been widely considered as potential candidates for preparing smart sensors, flocculant additives, and ion exchange materials.<sup>1–6</sup>

Since Alfrey et al. first reported the successful synthesis of a zwitterionic compound in 1950,<sup>7</sup> thousands of zwitterionic polymers have been synthesized in recent decades. The traditional method of synthesizing zwitterionic polymer is free radical polymerization. Using this method, Ehrlich et al.<sup>8</sup> synthesized methacrylic acid-*stat*-2-(dimethylamino)ethyl

methacrylate polymers later. Stille's group<sup>9,10</sup> firstly synthesized a zwitterionic polymer of poly-trimethylsilyl methacrylate (TMSMA) by anionic polymerization in the early 1970s. With the development of studies on polymerization theory and controlled polymerization method, several new polymerization methods such as group transfer polymerization (GTP),<sup>11</sup> n-methyl-2-pyrrolidone (NMP),<sup>12</sup> atom transfer radical polymerization (ATRP),<sup>13,14</sup> and reversible addition-fragmentation chain transfer polymerization (RAFT)<sup>15,16</sup> are found. A lot of zwitterionic polymers with specific structure and property are simply synthesized in moderate reaction systems with high efficiency. The property of zwitterion materials was mainly dependent on the chemical composition of polymer. A zwitterionic copolymer coupling hydrophilic and hydrophobic branches together possesses good affinity with both hydrophobic materials and water. It is compatible with most synthesized polymer materials for the hydrophobic interaction. Its solubility and solution behavior in water can be adjusted by controlling the hydrophilic/hydrophobic branch ratio and structure. The compatible copolymer has been widely used in surface modification and solution property adjustment area. Qian and coworkers synthesized a novel acrylamide and 4-vinylpyridine propylsulfobetaine (AMVPPS) zwitterionic copolymer and used it as flocculation in water treatment.<sup>5</sup> Baggerman and coworkers

**Table I.** The Composition of Reaction System for Synthesizing Compatible Zwitterionic p(MMA-MPDSAH) Copolymers with Different MPDSAH Branches

Type	MMA (mol)	MPDSAH (mol)	Zwitterionic content in the monomers (%)	AIBN (g)	Water (mL)/ Ethanol (mL)
PMMA	1.0	-	-	0.5	75/75
Polymer I	1.0	0.05	4.8	0.5	75/75
Polymer II	1.0	0.07	6.3	0.5	75/75
Polymer III	1.0	0.14	12.5	0.5	75/75
Polymer IV	1.0	0.25	20.0	0.5	75/75

prepared a kind of zwitterionic copolymer brushes grafted on silicon nitride. An excellent protein repellence of 99% was observed by coating the zwitterionic polymer on  $\text{Si}_x\text{N}_4$  surface.<sup>17</sup> Jiang and Zhang's groups utilized novel zwitterionic copolymers to prepare high antifouling and water permeability property by blending or surface grafting.<sup>18,19</sup> Zwitterionic copolymer material becomes more and more important focusing on the area of petroleum, chemical engineering, and new materials industry.

Membranes can separate solutions with high speed and low cost. It plays an important role in sewage treatment, product separation, and sea water desalination.<sup>20–22</sup> Membranes prepared by common materials such as PVDF, polyethersulfone (PES), and polysulfone (PSF) which possess good thermal stability, high mechanical strength, and chemical resistance are able to bear varieties of application circumstance, even in extreme environment.<sup>23</sup> Unfortunately, these materials have a common fatal flaw of hydrophobic which leads to serious membrane fouling. It reduces the efficiency and working life of membrane modules, resulting in an increase of cost in use.<sup>24</sup> It is necessary to enhance the hydrophilicity of membrane surface by an effective method.<sup>25</sup> One traditional method is to blend hydrophilic polymer like PEG and PVP with membrane materials. However, the vested hydrophilicity is temporary for the blended materials and is easily redissolved in water. It would be washed away slowly in application. Another effective way is to graft hydrophilic branches on the surface of membranes by surface polymeric methods. It is difficult to control and manufacture in industry.<sup>26,27</sup> Compatible zwitterionic block copolymer is hydrophilic. It has good affinity with hydrophobic material ensuring the hydrophilic branches in membranes steady. Membrane modified by zwitterionic block copolymer materials can obtain enduring hydrophilicity.<sup>28–30</sup>

[3-(Methacryloylamino)propyl]dimethyl (3-sulfopropyl) ammonium-hydroxide (MPDSAH) is a zwitterionic monomer. The polymeric material (PMPDSAH) is highly hydrophilic.<sup>31</sup> In this article, a compatible zwitterionic block copolymer of poly (methyl methacrylate [3-(methacryloylamino)propyl]dimethyl (3-sulfopropyl) ammonium-hydroxide) (p(MMA-MPDSAH)) was synthesized via free radical polymerization and blended with PVDF to prepare enduring antifouling membrane via thermally induced phase separation (TIPS) method. By control reactive monomer ratio, several zwitterionic block copolymers with different MPDSAH branch ratio were obtained and utilized to enhance the hydrophilicity of PVDF membrane. The chemical structure of p(MMA-MPDSAH) was characterized by gel

permeation chromatography (GPC) and Fourier transform infrared (FTIR). The antifouling ability was evaluated by BSA absorption experiment. The stable residue content was analyzed by elemental analysis. To our best knowledge, p(MMA-MPDSAH) was synthesized and used on PVDF membrane modification for the first time. The excellent hydrophilicity endows the PVDF/p(MMA-MPDSAH) blend membrane with good antifouling property and potential application in protein separation and medical purification.

## EXPERIMENTAL

### Materials

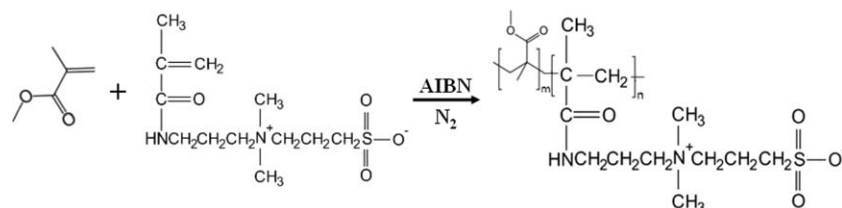
PVDF ( $M_w = 322,000$ , Daicel Chemical Industries, Japan) was used as the main material to cast membranes. Methyl methacrylate (MMA) supplied by Daicel Chemical Industries (Japan) was distilled before use. MPDSAH monomer and Azobisisobutyronitrile (AIBN) were purchased from Sigma Aldrich and used directly. Diethyl phthalate (DEP) and BSA purchased from Wako Pure Chemical Industries, Ltd. were utilized without any pretreatment.

### Synthesize of Compatible Zwitterionic Copolymer P(MMA-MPDSAH)

Four kinds of zwitterionic copolymers with different MPDSAH branch ratio were synthesized by varying MPDSAH/MMA ratio in polymeric reaction system using AIBN as initiator.<sup>31</sup> The composition of reaction solutions is shown in Table I. In a typical procedure, desired amount of MPDSAH and purified MMA were dissolved with deionized water/ethanol mixture in a 500-mL round-bottom flask to make a homogenous solution at room temperature. Nitrogen gas was continuously bubbled through the mixed solution for 10 min to eliminate oxygen before adding AIBN to initiate the reaction. The polymerization was carried out at 80°C for 10 h under gentle stirring. Scheme 1 shows the scheme for polymeric reaction. The products were collected and washed with water then chloroform for three times respectively. Finally, the copolymers were obtained after drying in vacuum for 24 h at 40°C and relevantly coded as Copolymer I, Copolymer II, Copolymer III, and Copolymer IV with the increasing of reactive MPDSAH/MMA ratio.

### Spinning of PVDF Hollow Fiber Membranes

The hollow fiber membranes were spun using PVDF as the main material with a batch-type extruder (Imoto Corp.) according to Ref. [32]. To prepare the casting solutions, measured amounts of PVDF, p(MMA-MPDSAH), and DEP with a fixed weight ratio of 27 : 3 : 70 were mixed in a vessel and heated to



**Scheme 1.** Synthesis of zwitterionic p(MMA-MPDSA) copolymers.

230°C for 4 h to obtain homogenous dopes. Prior to spinning, the dope temperature was decreased to 190°C after degassing. The homogeneous polymer solution was fed into a spinneret by a gear pump under a pressure of 0.25 MPa. The DEP bore fluid was heated to 190°C before feeding into the inner tube of the spinneret while the polymer dope was extruded into outer tube to fabricate hollow fiber membranes. The hollow fiber was coagulated into water bath at 40°C and taken up with a speed of 0.12 m/s by a winder. Each type of copolymers was spun with PVDF at the same condition. The prepared membranes were rinsed in large amount of water for a couple of days to remove the solvent and bore fluid completely and kept in water until use. All the membranes were prepared at the same condition.

### Characterization

The molecular weight ( $M_w$ ) and its distribution index ( $M_w/M_n$ ) of each synthesized p(MMA-MPDSA) were characterized by gel permeation chromatography (GPC, Shimadzu Co., Japan) using Poly(methyl methacrylate) (PMMA) as standards and *N*-methyl-2-pyrrolidone (NMP) as solvent at room temperature (25°C). FTIR spectroscopy of p(MMA-MPDSA) copolymer was recorded in the range of 4000–1000  $\text{cm}^{-1}$  with FTIR spectrometer (Alpha-E, Bruker). The morphology of the membranes was observed by scanning electron microscope (SEM, Hitachi Co., S-800) with an accelerating voltage of 20 kV. Samples were fractured in liquid nitrogen and dried by a freeze dryer (EYELA, FD-1000). The residue content of copolymer in PVDF membrane was obtained by measuring the weight percentages of C, N, O, and S elements on Elemental Analyzer (Systems Engineering Co., Japan). The BSA absorption behavior on membranes was conducted with quartz crystal microbalance (QCM) by casting prepared polymer solution on the Au sensor of microbalance. The water contact angle on the outer surface of hollow fiber membrane was measured with a contact angle meter (Kyowa Kaimenkagaku, CA-A) at room temperature (25°C).

## RESULTS AND DISCUSSION

### Characterization of P(MMA-MPDSA) Copolymers

GPC was an effective method to determine the molecular weight and its corresponding distribution index based on a standard molecule. Table II shows the GPC result of the synthesized p(MMA-MPDSA) by free radical polymerization. Under the degradation of AIBN initiator, amounts of free radicals were generated and induced both monomers to polymerize. PMMA was synthesized from MMA monomer only. Copolymers I, II, III, and IV were polymerized by connecting MMA monomer and MPDSA monomer. The molecular weights ( $M_w$ ) of PMMA, Copolymers I, II, III and IV were 22,000, 55,000, 56,000, 43,000, and 21,000, respectively. In regular, a high monomer concentration might accelerate the reaction and the

molecular weight of product would increase. But excess MPDSA went against the polymerization because of its long branches which increased steric hindrance of the reaction in this system. Four types of copolymer with different zwitterionic branch percentage were obtained. The  $M_w$  decreased while the zwitterionic branch contents increased as the increasing of MPDSA monomer concentration for the steric hindrance effect. The molecular weight distribution index ( $M_w/M_n$ ) was very narrow since this polymerization was living polymerization. Poly(MPDSA) has very high hydrophilic and dissolved in water easily. P(MMA-MPDSA) was amphiphatic for the combination of hydrophilic MPDSA and hydrophobic PMMA.

FTIR spectra of MPDSA, PMMA, and p(MMA-MPDSA) block copolymer are shown in Figure 1. It could be seen clearly that the characterized absorption peak of acyl (C=O) and ether (C—O—C) for PMMA was shown at 1758  $\text{cm}^{-1}$  and 1036  $\text{cm}^{-1}$  while strong peaks were displayed at 1209 and 1544  $\text{cm}^{-1}$  for MPDSA ascribing to symmetric and asymmetric stretch vibrations of sulfonate and C—N groups.<sup>33,34</sup> Both sulfonate and ether groups appeared in p(MMA-MPDSA) polymer, indicating that the two monomers had been combined together in the copolymer. This result demonstrated p(MMA-MPDSA) was successfully obtained by the polymerization of MPDSA and MMA monomers.

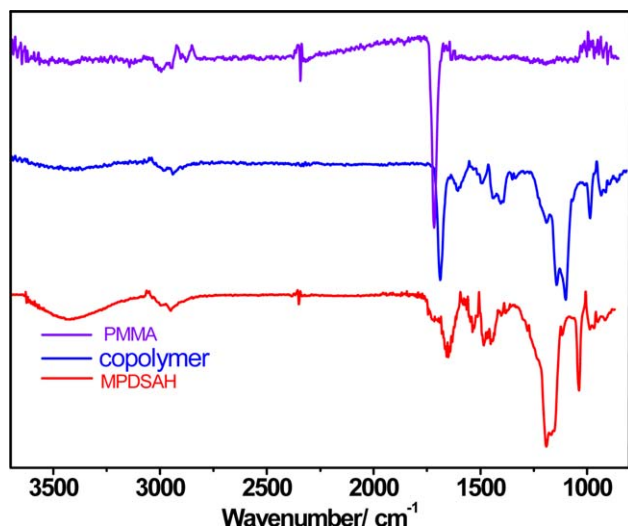
### Investigation of Membrane Morphology and Hydrophilic

Figure 2 shows the SEM images for the cross-section and outer surface of hollow fiber membranes fabricated by pristine PVDF and PVDF/p(MMA-MPDSA) blend. It was clear that a typical structure of TIPS membranes was observed in the cross-section that spherulites were formed according to solid-liquid phase separation theory in coagulation process. However, the size of spherulites decreased when introducing zwitterionic copolymer of p(MMA-MPDSA). This might attribute to the interaction

**Table II.** The  $M_w$  and  $M_w/M_n$  of Four Different Zwitterionic p(MMA-MPDSA) Copolymers Synthesized by Varying MMA/MPDSA Ratio

Type	Zwitterionic content (%)		GPC	
	Feed	Product	$M_w$	$M_w/M_n$
PMMA	-	-	22,000	1.61
Polymer I	4.8	4.6	55,000	1.72
Polymer II	6.3	6.1	56,000	2.15
Polymer III	12.5	12.1	43,000	2.11
Polymer IV	20	17.1	21,000	1.94
Poly (MPDSA)	-	-	6500	2.01





**Figure 1.** The FTIR spectra for MPDASH monomer, synthesized polymer IV, and pristine PMMA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

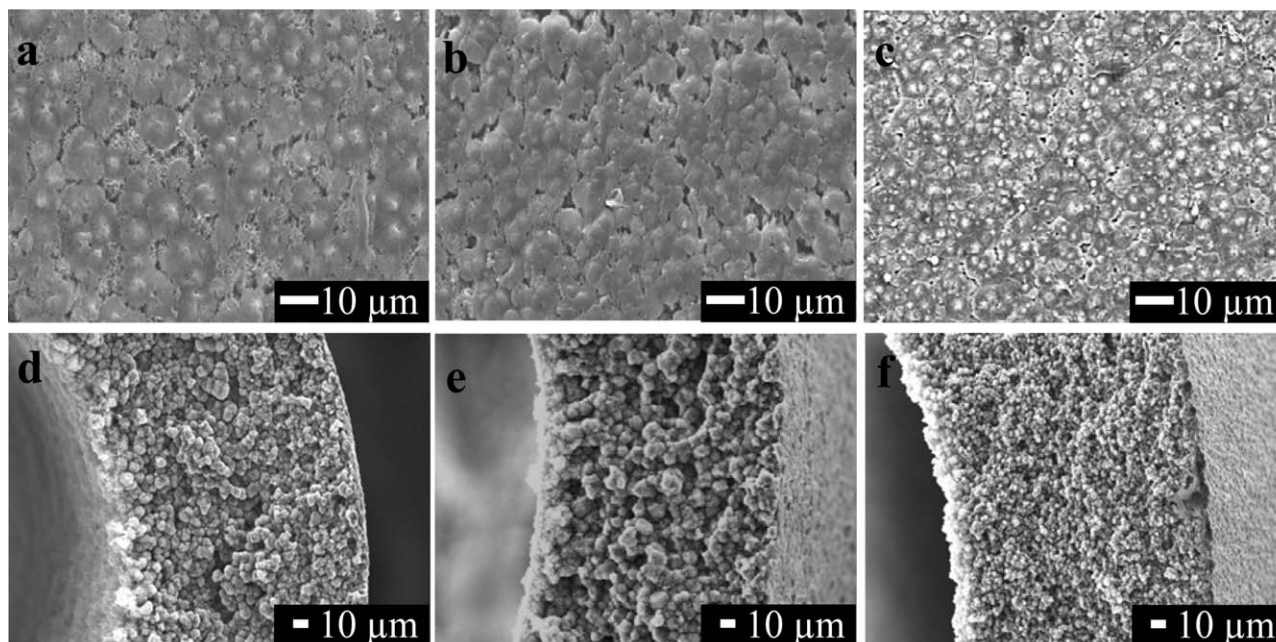
between PVDF and p(MMA-MPDASH) which increased the viscosity and decreased the crystallization temperature of spinning dope. It would restrain the growth of spherulites and thus favor the formation of crystal nucleus as phase separation progresses.<sup>35,36</sup> So the spherulite diameter diminished.

However, most hydrophilic additives in membranes were unstable and easily re-dissolved in water which would cause the hydrophilicity to lose in use. To study the stable residue content of p(MMA-MPDASH) polymers in membrane, we rinsed the prepared membranes vigorously and characterized the remained C, N, O, S element content by elemental analyzer (EA). The residue copolymer content was calculated from the result and

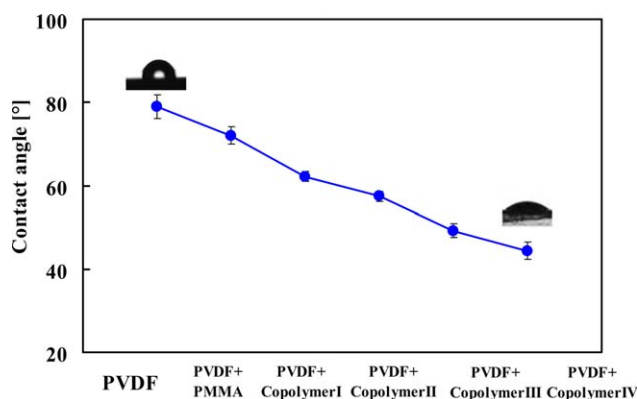
shown in Figure 3. All membranes were fabricated with the same content of copolymers. It was obvious that the remained polymer content decreased with the increase of the zwitterionic branch ratio in copolymers as zwitterionic MPDASH was hydrophilic. The residual content of Copolymer IV was the lowest since its zwitterionic MPDASH branch was the highest and its molecular weight was the smallest. It was still above 40% while that for Copolymers I and II approached to 80%.

The water contact angle on outer surface of hollow fiber membrane was measured with a contact angle meter at room temperature. Figure 4 shows that the contact angle had decreased obviously as the zwitterionic branch ratio increased in the added copolymers although the remained Copolymer IV content was the lowest. This was attributed to the definite high zwitterionic branch content. The combined MPDASH branch of Copolymer IV was almost four times than that of Copolymer I when the residue content was a half. The contact angle was lower than  $50^\circ$  for PVDF/Copolymer IV hollow fiber membrane. It was quite low compared to that of  $80^\circ$  for pristine PVDF membrane. That could be concluded that zwitterionic copolymer could improve the hydrophilicity of PVDF membrane surface.

In general, PVDF is hydrophobic. Zwitterionic copolymers are provided with both a hydrophobic chain and certain amount of hydrophilic branches.<sup>37</sup> PVDF and zwitterionic copolymers blended homogeneously and interaction occurred between the hydrophobic molecule chains. The hydrophilic branches in the additive had little affinity with PVDF molecular chains. The interaction force was increased with the decrease of hydrophilic branch ratio in copolymers. When the hydrophilic branch content was low, the hydration was weak and the interaction force could not dissolve zwitterionic copolymers. The hydrophilic additives would corrode away with water when the force was



**Figure 2.** The SEM images for the outer surface (a–c) and cross-section (d–f) of membranes fabricated by pristine PVDF only (a, d), PVDF/copolymer I (b, e) and PVDF/Copolymer III via TIPS method.

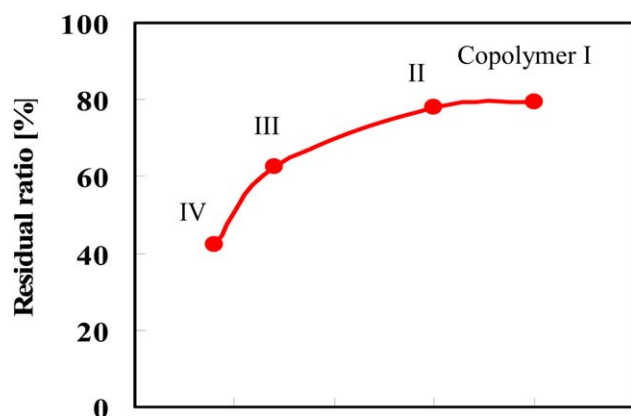


**Figure 3.** The variation of water contact angle on the outer surface of PVDF membrane and modified PVDF membranes with different polymer additives. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

enough to peel the added molecular off the main membrane material. Copolymer IV possessed the highest zwitterionic branch content and lowest molecular weight in all copolymers. It corroded seriously, leading to a low residue content of 40% in membranes. In a word, the synthesized zwitterionic p(MMA-MPDSAHA) can remain in membranes stably. Membranes modified by it are hydrophilic and capable of resisting protein fouling enduringly.

#### Protein Adsorption Behavior of Membranes

BSA was easily absorbed on hydrophobic surface and used as the model protein to study the antifouling ability of membranes. The BSA adsorption behavior on each polymer surface and different membranes was investigated by QCM. PVDF and PMMA were used as the control. Figure 5 shows the adsorbed BSA behavior on PVDF, PMMA, zwitterionic Copolymer IV, and membranes modified with different copolymers. In Figure 5(a), Copolymer IV adsorbed about  $1.5 \text{ mg/m}^2$  in 20 min while it was about 3.5 and  $5 \text{ mg/m}^2$  for PMMA and PVDF. Similar case occurred in different membranes in Figure 5(b) that the stable BSA adsorbed content in 20 min was only  $1.5 \text{ mg/m}^2$  for

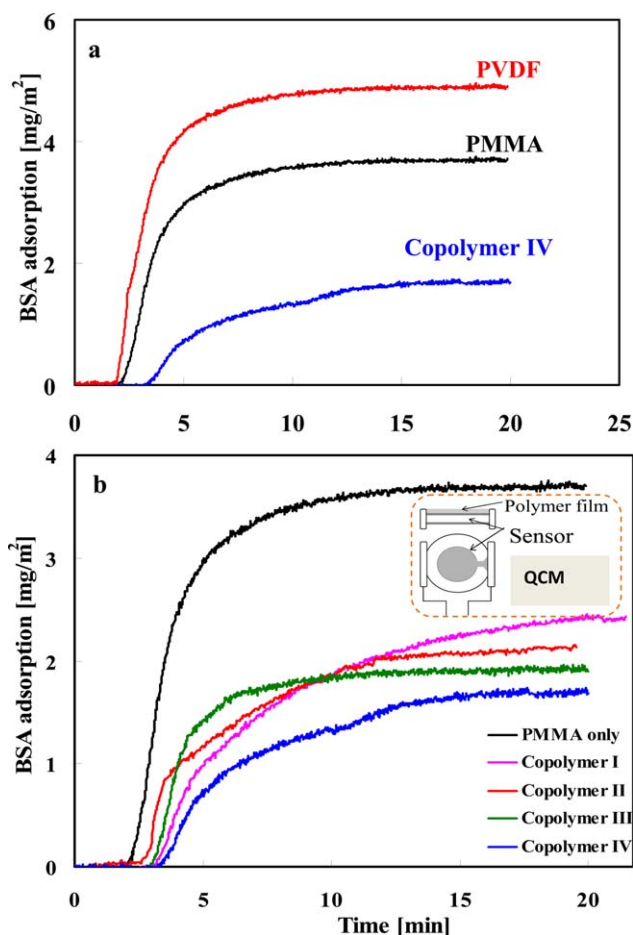


**Figure 4.** The residual ratio of different zwitterionic polymers in PVDF membranes after washing the membranes with large amount of water. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membrane modified by Copolymer IV while it was about  $3.5 \text{ mg/m}^2$  for PMMA/PVDF membrane. The adsorbed BSA content was increased as the increase of the hydrophilicity of added copolymers. The BSA absorbing ability had diminished about 50% with only 3% zwitterionic copolymers in PVDF membrane.

#### CONCLUSION

Novel zwitterionic copolymer p(MMA-MPDSAHA) was synthesized by free radical polymerization in water phase suspension. GPC results demonstrated the reaction was successful and four types of copolymers with different MPDSAHA branch ratio were obtained. PVDF/p(MMA-MPDSAHA) blend membranes with enhanced hydrophilic property were fabricated by TIPS process with 3% zwitterionic copolymers in spinning dope. It was found that the zwitterionic copolymer was interacted with main materials, leading to a decrease of spherulite diameter in the cross-section of membranes. The residue content of copolymer in membrane was characterized by Element Analysis after suffering vigorous rinsing. The calculated content of remained copolymer was decreased as the increasing of zwitterionic branch ratio in copolymers while the contact angle of modified



**Figure 5.** The plot of adsorbed BSA contents as a function of time on membranes fabricated by individual polymers (a) and modified PVDF with different types of p(MMA-MPDSAHA) (b). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

membrane surface was decreased resulting from a definite high zwitterionic branch content added in membranes. P(MMA-MPDSA)H possessed good affinity with PVDF material for its hydrophobic main chains. Its residual content was over 40% at vigorous rinsing and able to reach 80% by controlling the content of hydrophilic branches. In addition to p(MMA-MPDSA)H, the membrane hydrophilicity had improved obviously. The BSA absorption behavior corresponded to the hydrophilicity of membrane surface. It had cut from 3.6 mg/m<sup>2</sup> for pristine PVDF membrane to 1.6 mg/m<sup>2</sup> for PVDF/Copolymer IV in 20 min. The modified membranes were capable of resisting absorption fouling effectively. The zwitterionic copolymer with special structure improved the antifouling property of membranes enduringly. It could be used in protein separation and medical purification.

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