

Poly(*N,N*-dimethylaminoethyl methacrylate) Grafted Poly(vinyl chloride)s Synthesized *via* ATRP Process and Their Membranes for Dye Separation^{*}

Li-feng Fang, Na-chuan Wang, Ming-yong Zhou, Bao-ku Zhu^{**},
Li-ping Zhu and Angelin Ebanezar John

Key Laboratory of Macromolecular Synthesis and Functionalization (Ministry of Education), Engineering Research Center of Membrane and Water Treatment (Ministry of Education), Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China

Abstract To functionalize poly(vinyl chloride) (PVC) for various applications, monomers containing tertiary amine group are incorporated into PVC *via* atom transfer radical polymerization (ATRP) initiated by the labile chlorines in their backbones. The kinetics of synthesis was carefully investigated, and it is proven that the grafting polymerization process can be effectively controlled by regulating the reaction time. The membranes are fabricated using PVC and copolymers by non-solvent induced phase separation (NIPS) process. The hydrophilicity and pore structure of copolymer membranes were enhanced as well, these membranes are endowed with positive charge. When PDMA% (*i.e.*, the PDMA weight percentage in copolymer) is 31.1%, the flux and Victoria blue B rejection are $26.0 \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$ (0.5 MPa) and 91.2%, respectively. Thus, the newly synthesized polymer is proven to be a promising material for dye separation with positive charges.

Keywords: Poly(vinyl chloride); Poly(*N,N*-dimethylaminoethyl methacrylate); Non-solvent induced phase separation; Dye separation.

INTRODUCTION

Poly(vinyl chloride) (PVC) is one of the most important commercial plastics in the world. It is widely used in various applications including rigid pipes, flooring, window frames and filtration materials^[1, 2] due to its low cost, stiffness, excellent resistance towards acid, base and solvent. Emulsion and suspension polymerization technologies are the preferentially used methods in industries for PVC production. Although many kinds of monomers can be introduced into PVC backbone by these polymerization processes, the major aim is to synthesize the inner plasticizer copolymers^[3–5]. The monomers like ethylene or propylene are non-polar and thus cannot be dissolved in water, which helps them to copolymerize with vinyl chloride in the same medium. However, it is difficult to introduce the polar monomers (especially for water soluble ones) into PVC backbone *via* copolymerization, owing to the different partition coefficient of the monomers in dispersing agent (water) and organic phase. Therefore, it is critical to functionalize PVC by other methods. Moulay^[6] has reviewed the various possibilities to modify PVC such as nucleophilic and radical substitution, elimination, grafting polymerization by cationic and radical polymerization based on the presence of labile chlorines (*i.e.*, tertiary and internal allylic chlorines) in PVC. Since Wang and Matyjaszewski^[7] found ATRP process in 1995, the reaction has been performed in PVC modification started by Percec *et al.*^[8] using the labile chlorines as the initiator.

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^{**} Corresponding author: Bao-ku Zhu (朱宝库), E-mail: zhbk@zju.edu.cn

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From then on, many investigators grafted methyl methacrylate, butyl acrylate^[9], styrene^[8], *etc.*, onto the PVC backbone using ATRP process. The modified PVC materials are mainly used in gas separation^[10, 11] and biomedical devices^[6] but very few are used as membranes for water filtration, especially for nanofiltration membranes.

In IUPAC definition, the nanofiltration membrane is defined as the following: “Pressure-driven membrane-based separation process in which particles and dissolved macromolecules smaller than 2 nm are rejected”^[12]. It is prepared for decades by various techniques including interfacial polymerization^[13, 14], surface grafting^[15, 16], surface coating^[17, 18] and so on. Although non-solvent induced phase separation (NIPS) process is mainly adopted to prepare microfiltration and ultrafiltration membranes, it is also an effective method for nanofiltration membranes^[19]. By using nanofiltration membranes, organic compounds with low molecular weight (200–1000 g·mol⁻¹), divalent ion and hydrolyzed reactive dyes could be effectively removed^[20].

In this work, a novel nanofiltration membrane for dye separation has been primarily explored *via* a one-step NIPS process. The membrane is made up of a novel PVC based copolymer, which is synthesized by grafting poly(*N,N*-dimethylaminoethyl methacrylate) (PDMA) chains onto PVC by ATRP process, which has been adopted as the common technique for polymer synthesis and membrane modification^[21–26]. On the one hand, due to the protonation ability of grafted PDMA chains, the hydrophilicity of membranes is improved compared to pure PVC membranes, which in turn promotes the permeability of membranes. On the other hand, the PDMA chains could be partially quaternized^[27] such that the membranes are endowed with positive charges on their surfaces. This will effectively prevent the positively charged dye from permeation according to Donnan effect. The synthesis process and kinetics of PVC-*g*-PDMA were carefully investigated. Here, victoria blue B (VBB) ($M_n = 506 \text{ g}\cdot\text{mol}^{-1}$) with positive charge and a diameter of 1.01 nm is used as the model dye molecule. In addition, the thermal resistance, morphology, surface chemical compositions, wettability, mechanical properties, surface charge, permeability and VBB separation performances were studied.

EXPERIMENTAL

Materials

The PVC resin (PVC1300) was obtained from Qilu Petrochemical Company (China). *N,N*-dimethylaminoethyl methacrylate (DMAEMA) was bought from Energy Chemical Co., Ltd. (China), which has been purified by vacuum distillation and stored at –18 °C until use. CuCl was purchased from Sinopharm Chemical Reagent Co., Ltd. (China), cleaned with acetic acid and ethanol several times and then dried under low pressure before use. Pentamethyldiethylenetriamine (PMDETA) was supplied by Sigma-Aldrich Co., Ltd. and used as received. Victoria blue B (VBB, 506.1 g·mol⁻¹) was bought from Aladdin Reagent Co. (China). *N*-methyl pyrrolidone (NMP), tetrahydrofuran (THF) and other regular reagents were obtained from Sinopharm Chemical Reagent Co., Ltd. (China) and used directly without further purification.

Synthesis of Graft Copolymer PVC-*g*-PDMA

PVC-*g*-PDMA has been synthesized *via* a single-step ATRP process utilizing the labile chlorines (*i.e.* allylic and tertiary chlorines) (Fig. 1). The typical synthesis process is described as follows. At first, the PVC resin is dissolved in NMP in a three-necked flask and then the reagents DMAEMA, PMDETA and CuCl (DMAEMA/PMDETA/CuCl = 100/1/1, mol/mol/mol) are introduced into the flask. The mixture is stirred and bubbled with dry nitrogen continuously for 30 min at 0 °C to expel the oxygen. Then the ATRP reaction is carried out at 65 °C for predetermined time intervals under nitrogen atmosphere. After polymerization, the solution is diluted with THF and passed through a silica column to remove copper. The resulting filtrate is precipitated in deionized water. Then this graft copolymer is further purified by dissolving in THF and precipitating in the deionized water several times. Finally, the resultant product is dried by a lyophilization process.

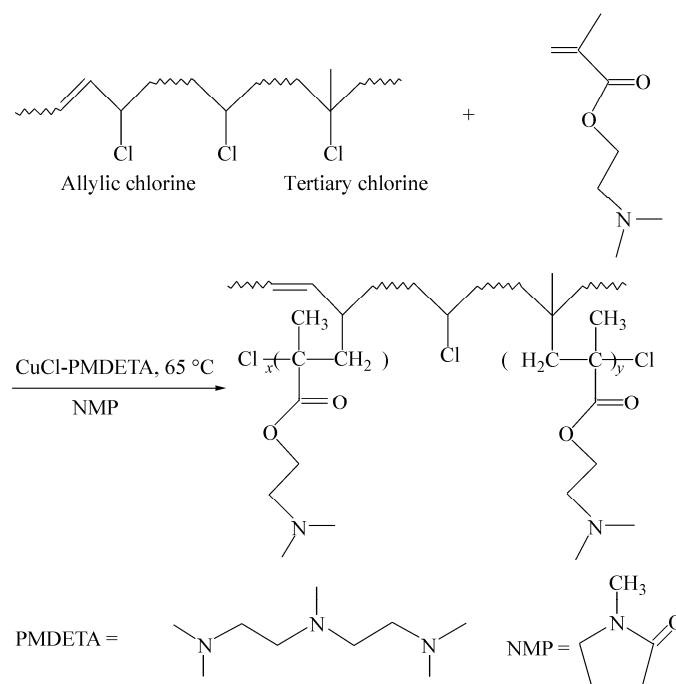


Fig. 1 The synthesis route of PVC-g-PDMA graft copolymer *via* ATRP process utilizing the labile chlorines (*i.e.* allylic and tertiary chlorines)

Preparation of Membranes

PVC and PVC-g-PDMA membranes were prepared by traditional non-solvent induced phase separation (NIPS) process. The polymer was first dissolved in NMP to form a homogenous solution (15 wt%). Then using a steel knife the solution was spread on a clean glass plate with a thickness of 250 μm . This solution film was then transferred into the deionized water at 30 °C. After complete coagulation, the resultant membrane was rinsed with deionized water to remove the residual solvent. These newly-prepared membranes were dried at room temperature for further characterization.

Characterizations of PVC-g-PDMA Copolymer

The chemical compositions of the copolymer were analyzed by Fourier transform infrared (FTIR) spectroscopy and proton nuclear magnetic resonance (^1H -NMR) spectroscopy. The FTIR spectra were collected from 400 cm^{-1} to 4000 cm^{-1} using a Bruker vector 22 Fourier transform infrared spectrometer with the KBr pellet. The NMR spectra were recorded on a Varian Unity Plus 300/54 NMR spectrometer at 40 °C in d_7 - N,N -dimethyl formamide (DMF). The molecular weights and polydispersity index (PDI) were determined by gel permeation chromatography (GPC, Waters 510 HPLC pump-Waters Styragel columns-Waters 410 differential refractometer) at 40 °C using DMF as an eluent. For this process, polymer solutions with a concentration of 3 $\text{mg}\cdot\text{mL}^{-1}$ in DMF were used. The GPC system was calibrated by polystyrene with narrow PDI.

Characterizations of the Membrane

The morphology of the membrane was observed using a scanning electron microscope (SEM, Hitachi S4800, Japan) after gold-sputtering. Prior to the cross section observation, the membranes were fractured in liquid nitrogen. The surface chemical compositions were analyzed by attenuated total reflectance Fourier transform infrared (ATR-FTIR, Nicolet NEXUS 6700 spectrometer, Thermo Fisher Scientific, US) and X-ray photoelectron spectroscopy (XPS, Escalab 250Xi, Thermo Scientific, UK). Water contact angles were determined at 25 °C using the Dataphysics Instruments (OCA20, Germany) in a sessile drop model. An average of at least 6 measured values is taken as the final value. The thermal resistance of the membrane was characterized using differential scanning calorimetry (DSC, TA Instruments Q200, US). This measurement was

carried out in a temperature range from $-50\text{ }^{\circ}\text{C}$ to $150\text{ }^{\circ}\text{C}$ at a heating rate of $10\text{ K}\cdot\text{min}^{-1}$. The zeta potential (ζ , mV) is calculated according to the Helmholtz-Smoluchowski equation (1)^[28, 29],

$$\zeta = \frac{dE_s}{dP} \times \frac{\eta}{\varepsilon\varepsilon_0} \lambda_0 \quad (1)$$

where E_s is the streaming potential, P is the hydrodynamic pressure in the tunnel, η is the liquid viscosity, ε_0 is the vacuum permittivity, ε is the dielectric constant of the electrolyte and λ_0 is the specific conductivity of the bulk liquid. The zeta potential was experimentally determined using an electrokinetic analyzer (Anton Paar GmbH SurPASS, Austria). The test was carried out in $1\text{ mmol}\cdot\text{L}^{-1}$ KCl solution at $25\text{ }^{\circ}\text{C}$. A series of zeta potential measurements were performed at different pH environments. That is the pH of solution is changed from 4 to 10 by adding $0.05\text{ mol}\cdot\text{L}^{-1}$ HCl and $0.05\text{ mol}\cdot\text{L}^{-1}$ NaOH. The filtration performances were tested on a Millipore UF stirred cell (XFUF047) at room temperature. The water flux (J_w , $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$) of tested membrane was calculated by equation (2).

$$J_w = \frac{V_w}{S \times t} \quad (2)$$

where V_w is the volume of permeate, S and t are the effective filtration area ($S = 15\text{ cm}^2$) and testing time (h), respectively. Afterwards the water was changed to VBB solution of $25\text{ mg}\cdot\text{L}^{-1}$ for separation test. The permeated solution was collected after 2 h. Then the concentration of the feed (c^{feed}) and the permeate (c^{permeate}) solutions were measured using UV-Vis spectrometer (HP 8453, USA) at a wavenumber of 599 nm . The VBB rejection ($R_{\text{VBB}}(\%)$) was calculated by the following equation.

$$R_{\text{VBB}}(\%) = \left(1 - \frac{c^{\text{permeate}}}{c^{\text{feed}}}\right) \times 100 \quad (3)$$

RESULTS AND DISCUSSION

Synthesis of PVC-g-PDMA Graft Copolymer

The reaction route for the synthesis of PVC-g-PDMA *via* ATRP process is illustrated in Fig. 1. Generally, compared to the labile chlorines (about 1–2 atoms per 1000 monomer units^[30]), the C–Cl bonds in PVC backbones are too strong to break. So the labile chlorines would act as the initiation site for graft copolymerization of PVC during copper-mediated ATRP^[9–11, 31]. The synthesized copolymers were identified using FTIR and ^1H -NMR spectroscopy techniques. Compared with the IR spectrum of PVC in Fig. 2(a), characteristic peaks at 1727 cm^{-1} and 1147 cm^{-1} which correspond to C=O stretching vibration and C–N stretching vibration^[32–34], respectively, appear in the spectrum of the graft copolymer. This primarily proves the successful synthesis of PVC-g-PDMA. The ^1H -NMR spectra for PVC and PVC-g-PDMA are shown in Fig. 2(b). The spectrum of PVC exhibits peaks at $\delta = 4.54$ and 2.32 , which are ascribed to the $-\text{CClH}-$ and $-\text{CH}_2-$ protons in PVC chain^[35], respectively. The peaks at $\delta = 2.75$, 2.91 and 8.02 are attributed to the deuterated solvent (DMF). While the spectrum of graft copolymer exhibits many new peaks at $\delta = 0.84$ – 1.22 , 1.81 – 2.05 , 2.28 , 2.59 and 4.10 . They are assigned to $-\text{C}-\text{CH}_3$ (c), $-\text{CH}_2-$ (d), $-\text{CH}_2-\text{N}-$ (f), $-\text{O}-\text{CH}_2-$ (e) and $-\text{N}-\text{CH}_3$ (g), respectively (Fig. 2b)^[36], indicating the existence of PDMA in the copolymer. The above results provide a strong evidence that the graft copolymerization has been performed successfully.

For further investigation of the synthesis process, a series of graft copolymers are prepared with different reaction time (0.5 h, 1.0 h, 2.0 h and 4.0 h), and these copolymers are designated as PDMA0.5, PDMA1.0, PDMA2.0 and PDMA4.0, respectively. The number average molecular weight (M_n), PDI (M_w/M_n) and the chemical constitution (*i.e.* PDMA% means the PDMA weight percentage in copolymer) of PVC and copolymers have been determined by GPC and ^1H -NMR. The corresponding results are shown in Table 1 and Fig. 3. Each elution curve is characterized by only one peak as can be seen in Fig. 3, which means the substance is a sort of copolymer rather than a blend. This result provides another strong evidence for the successful synthesis of PVC-

g-PDMA. With the increase in reaction time from 0.5 h (PDMA0.5) to 4 h (PDMA4.0), the GPC curves shift towards the high molecular weight side and the M_n of copolymers increases from $11.5 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$ to $18.0 \times 10^4 \text{ g}\cdot\text{mol}^{-1}$. In addition, PDI of copolymers increases from 2.18 to 3.01. According to $^1\text{H-NMR}$ results, the PDMA chains are obviously incorporated into PVC such that PDMA% reaches up to 56.9% when reaction time is 4 h.

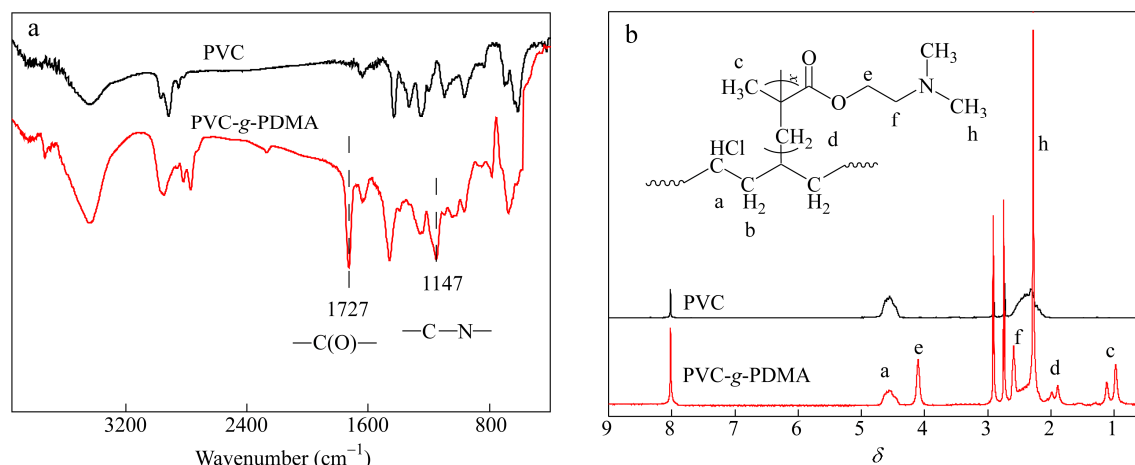


Fig. 2 (a) The IR spectra of PVC and PVC-g-PDMA and (b) the $^1\text{H-NMR}$ spectra of PVC and PVC-g-PDMA in d7-dimethyl formamide

Table 1. The molecular weight, PDI and compositions of PVC and its copolymers

Polymer	Time (h)	M_n^a	PDI	PDMA ^b (%)	M_n^b
PVC	—	79300	2.10	—	—
PDMA0.5	0.5	114800	2.18	20.9%	100200
PDMA1.0	1.0	121700	2.34	31.1%	115100
PDMA2.0	2.0	151700	2.89	53.9%	172000
PDMA4.0	4.0	180400	3.01	56.9%	184000

^a Determined from GPC results; ^b Calculated according to $^1\text{H-NMR}$ results

The kinetics of ATRP process are also investigated at 65 °C in the presence of NMP. As it can be seen from Fig. 3, an approximately linear increase in M_n with the conversion of monomers and a linear increase in $\ln([M]_0/[M])$ with time during the reaction are observed. These results suggest that the grafting copolymerization process is controllable within a predefined time period, which accords to the live character of ATRP process at low conversions. The above analysis reveals that various copolymers with different compositions could be easily synthesized by controlling the reaction time. It should be noteworthy that the molecular weight of PVC-g-PDMA is not very suitable for determination by GPC because the hydrodynamic volume of the copolymer cannot truly reflect its molecular weight. However, it is found that the molecular weights of copolymers calculated from NMR results are similar to those detected by GPC as shown in Table 1. The reason is mainly attributed to the number of graft chains present in these copolymers. According to the previous publications^[30], there are about 1–2 labile chlorines per 1000 VC units, that means each PVC macromolecule contains 1.3–2.6 grafting chains (the number of repeated units in this work is about 1300). Such kind of graft copolymer is more similar to linear molecule or double/triple block copolymer and so the molecular weight of the copolymer determined by GPC can be approximated to the real one. Therefore, the GPC results of copolymers are adopted in this work.

The Thermal Resistance of PVC and Copolymer Membranes

To investigate the thermal resistance of the new copolymer and its membranes, the glass transition temperature (T_g) of PVC and copolymer membranes has been determined by DSC. Figure 4 shows the DSC curves of PVC membrane and PVC-g-PDMA copolymer membranes. The membranes are labeled as M0, M1, M2, M3 and M4

for those prepared from PVC, PDMA0.5, PDMA1.0, PDMA2.0 and PDMA4.0, respectively. From Fig. 4, it can be seen that only a single T_g has been observed for PVC and all the copolymer membranes, which implies an excellent compatibility of PVC and PDMA. As it is well known, the T_g of PDMA is about 19 °C, but the T_g of PVC in this work is about 86.0 °C. When the PDMA% increase from 0 to 56.9%, T_g drops to 57.8 °C, which indicates the thermal resistance variation of copolymer membranes with the increase in PDMA%. However, the membranes are always used at relatively low temperatures (below 45 °C). Thus, the copolymer membranes made from PVC-g-PDMA are suitable for water treatment.

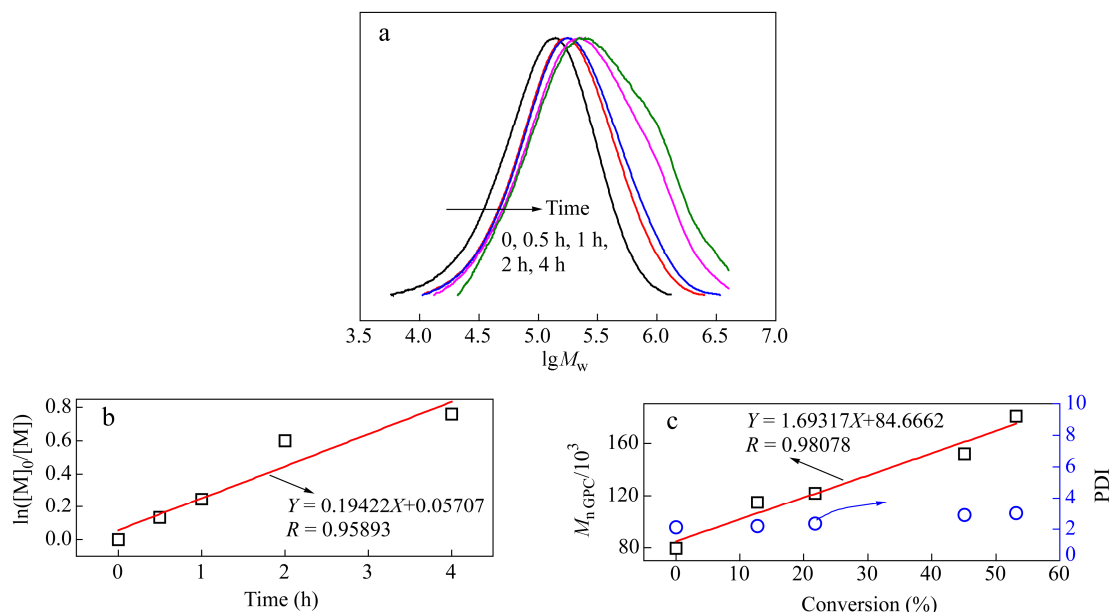


Fig. 3 (a) The GPC curves of PVC-g-PDMA with different reaction time (0, 0.5 h, 1 h, 2 h and 4 h); (b) kinetic plots of $\ln([M]_0/[M])$ versus time and (c) plot of number average molecular weights (M_n) and PDI (M_w/M_n) versus conversion (%) for ATRP process at 65 °C in NMP (Conditions: $[PVC] = 0.05 \text{ g}\cdot\text{mL}^{-1}$ and $DMAEMA/CuCl/PMDETA = 100/1/1$, mol/mol/mol.)

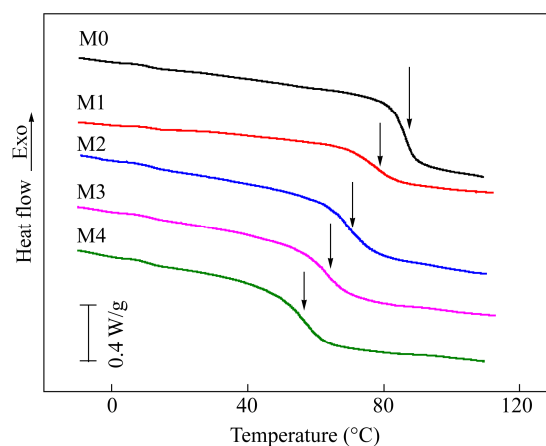


Fig. 4 DSC curves of M0, M1, M2, M3 and M4

Morphology of Membranes

The surface and cross sectional morphologies of the membranes (M0, M1, M2 and M3) are visualized by SEM and are depicted in Fig. 5. It can be clearly seen that, the pure PVC membranes (M0) as well as the copolymer

membranes (M1, M2 and M3) exhibit a typical asymmetric structure containing a dense top layer with the thickness of about 1 μm and a finger-like sub-layer. Usually, the dense top layer acts as the functional layer for permeation and filtration while the porous bulk layer is responsible for their mechanical property^[37]. In the case of M0, the finger-like pore cannot reach the bottom of membranes, which would further increase the resistance for water permeation. While for copolymer membranes, due to the introduction of hydrophilic PDMA chains into the membranes, the amphiphilic copolymer might be expected to increase the affinity between the copolymer and coagulation bath. This in turn accelerates the solvent-nonsolvent exchange and results in instantaneous de-mixing to form macrovoids^[38]. Thus the finger-like pores are fully developed and are close to the bottom. Compared to pure PVC membrane, the top surface of copolymer membranes are relatively dense with fewer and smaller pores on the surface.

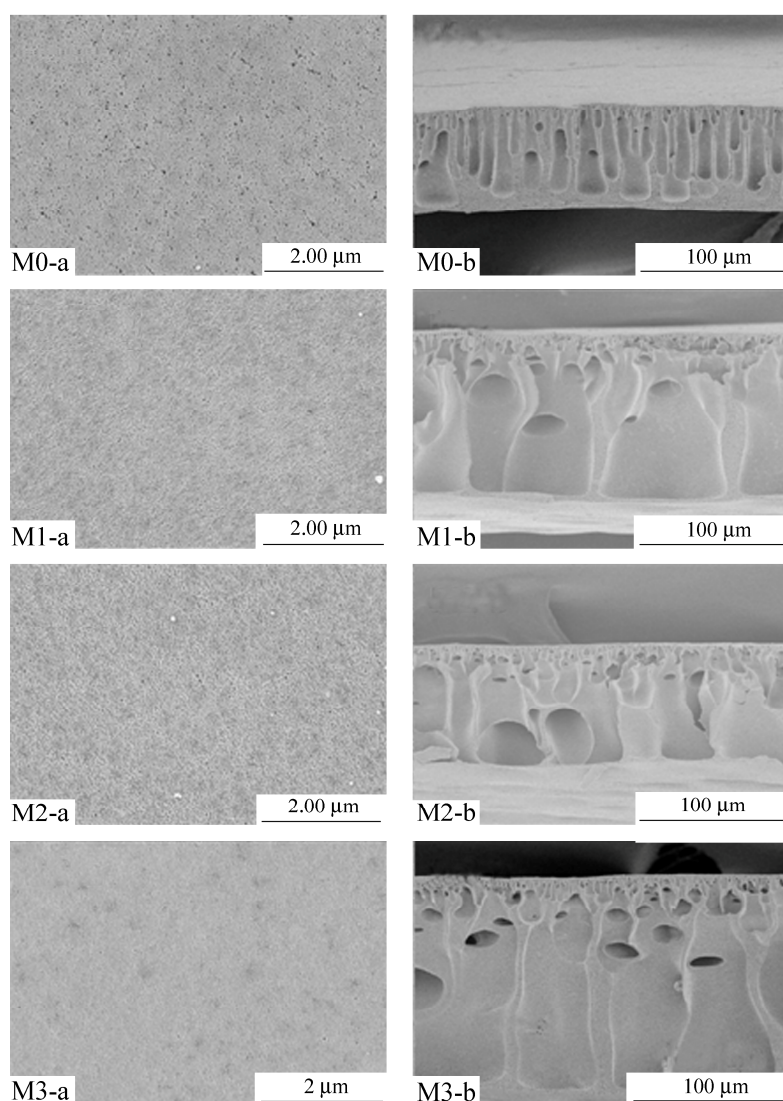


Fig. 5 The top surface (a) and cross section (b) of PVC membrane (M0) and copolymer membranes (M1, M2 and M3)

Surface Chemical Compositions

The surface chemical compositions of the membranes (M1, M2 and M3) were characterized by ATR-FTIR and XPS. The results are shown in Fig. 6. As can be seen in ATR spectra, the peak at 1727 cm^{-1} corresponds to the stretching vibration of carbonyl group in PDMA chains. For the better judgement of the surface PDMA content

of copolymer membranes, the peak at 1250 cm^{-1} (representing the characteristic adsorption peak of PVC) was normalized. It indicates the intensity of the peak (1727 cm^{-1}) increases with the PDMA% in the copolymer. The detail surface chemical compositions were listed in Table 2 by XPS. The increasing O and N contents in surface also indicates increasing PDMA content in surface with the augment of PDMA% in the copolymer. The elevated PDMA content in the surface would be further beneficial for the improvement of hydrophilicity and permeation.

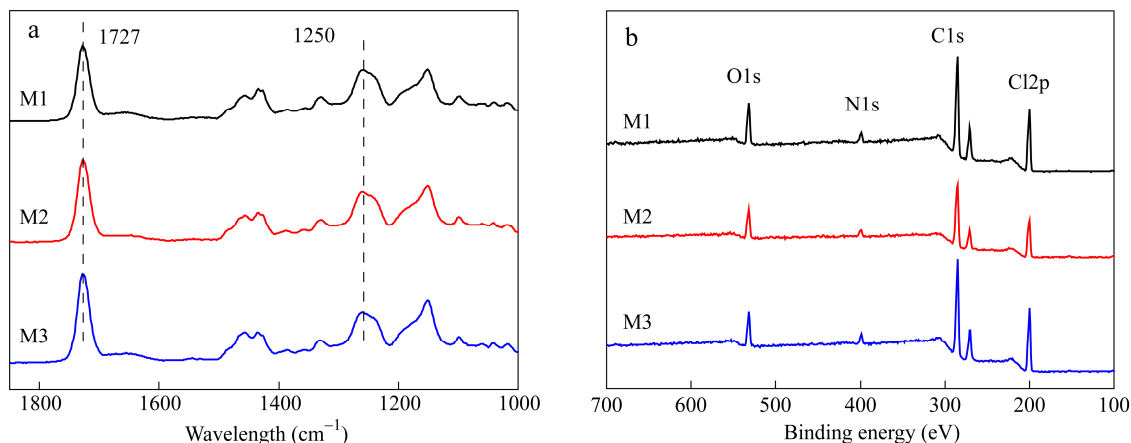


Fig. 6 (a) The ATR-FTIR and (b) XPS spectra of PVC-g-PDMA membranes (M1, M2 and M3)

Table 2. The data of full analysis of PVC-g-PDMA membranes

Sample ID	C (mol%)	O (mol%)	Cl (mol%)	N (mol%)
M1	68.51	12.37	14.81	4.31
M2	68.44	13.01	13.56	4.98
M3	69.32	14.47	9.62	6.58

Membrane Surface Wettability

The surface wettability of the membrane is the critical factor for membrane permeability, which is determined by the water contact angle on the surfaces. The results from the present measurements are shown in Fig. 7. Accordingly, the pure PVC membrane (M0) shows a hydrophobic property, whose water contact angle is about 90° . For the membranes fabricated from the copolymers (M1, M2 and M3), the static water contact angles decrease. That is the static contact angles are lower than 80° and so the water droplets tend to spread on the surface. In addition, it is well known that DMAEMA contains both the tertiary amine group as well as the carbonyl group. So the hydrogen-bonding interaction between the polar groups (*i.e.* tertiary amine group and carbonyl group)^[39] would help PVC-g-PDMA copolymers to be wetted in water, which further enhances hydrophilicity of the membranes. Moreover, the decay rate of contact angles on copolymer membranes (M1, M2 and M3), especially with a high PDMA%, is much higher than that of PVC membrane (M0) (Fig. 7b). It can be noticed that, the contact angle on M0 decreases from 87.3° to 85.5° after 80 s, while the contact angle on M3 decreases from 79.5° to 64.8° . The reason might be that the hydrophilicity of the membranes is enhanced on their surface as well as in the pores such that the increased hydrophilicity facilitates water to diffuse into the membrane. This improvement can be expected to benefit the filtration performances of the membranes.

Surface Charge of the Membranes

Surface charge is crucial in nanofiltration membranes. This is important not only for the transport of charged components but also for the uncharged components^[40], so the surface charge of the membranes was also characterized. The surface charge is determined by streaming potential measurements. The zeta potentials plotted against pH of PVC and copolymer membranes are displayed in Fig. 8. As expected, the zeta potential at pH 7.0 of PVC membrane is negative and the potentials for copolymers are positive. Also the isoelectric point of the membranes shifts from 5.5 to about 9.0, which is due to the introduction of PDMA chains into PVC. Owing to

the lone pair of electrons in the nitrogen atom present in PDMA, the copolymer tends to combine protons in aqueous solution and be partially quaternized^[41, 42]. Generally, the membranes with more PDMA% would possess more positive charge. During filtration experiment, this positive charges on the surface would be beneficial for positive dye separation due to the electrostatic repulsion.

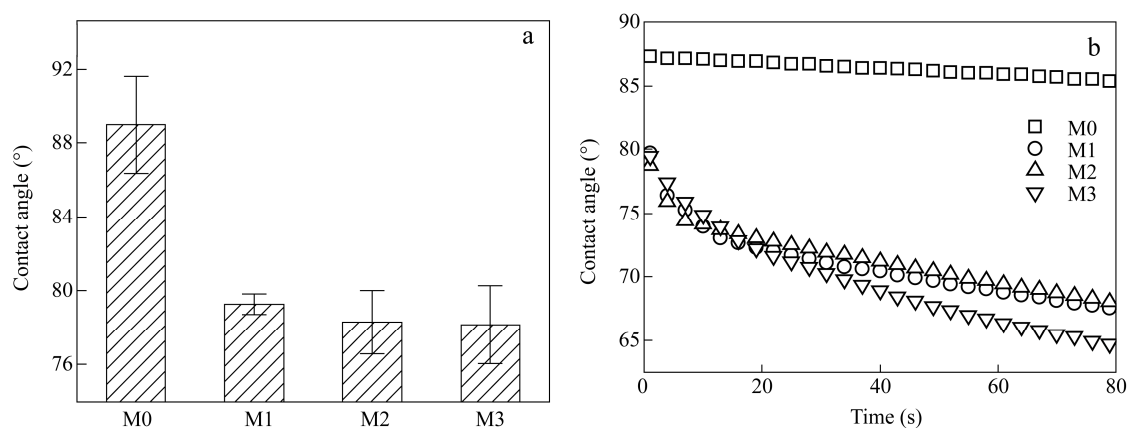


Fig. 7 The static (a) and time dependence (b) of contact angles on M0, M1, M2 and M3

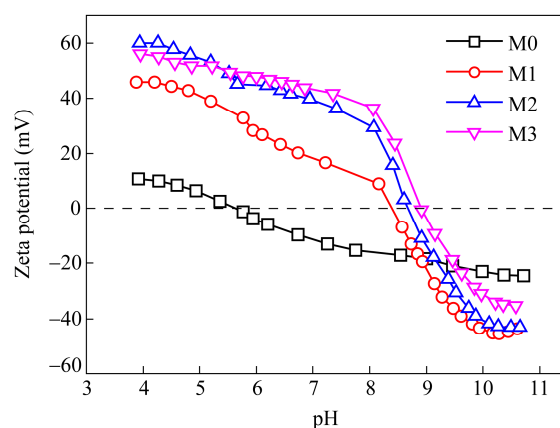


Fig. 8 Zeta potentials plotted against pH of pure PVC membrane (M0) and copolymer membranes (M1, M2 and M3)

Filtration Performances

To investigate the permeability and separation performances of PVC and its copolymer membranes, the water permeation fluxes and VBB rejection of membranes were primarily measured. They are shown in Fig. 9. The water flux of pure PVC membrane (M0) is 0. But for the copolymer membranes, the flux of M1, M2 and M3 are 13.5, 26.0 and 40.5 L·m⁻²·h⁻¹, respectively, when the transmembrane pressure is 0.5 MPa. This improved permeability of the copolymer membranes depends mainly on the membrane structure and membrane hydrophilicity^[43]. For instance, as observed in Fig. 5, the finger-like pores of M0 are not sufficiently developed and there is a thickness of about 10 μm of PVC matrix near the bottom surface of the membrane, which would increase the hydraulic resistance. The hydrophobicity of PVC material further prevents water from diffusing into the micropores and thus leads to 0 water flux of the membrane. While for the copolymer membranes, the fully developed finger-like pores in the cross section of M1–M3, good interconnectivity of the membrane matrix (Fig. 5) as well as the enhanced surface hydrophilicity (Fig. 7) will favor water diffusion. Among the resultant membranes, M3 is more hydrophilic, resulting in the larger flux.

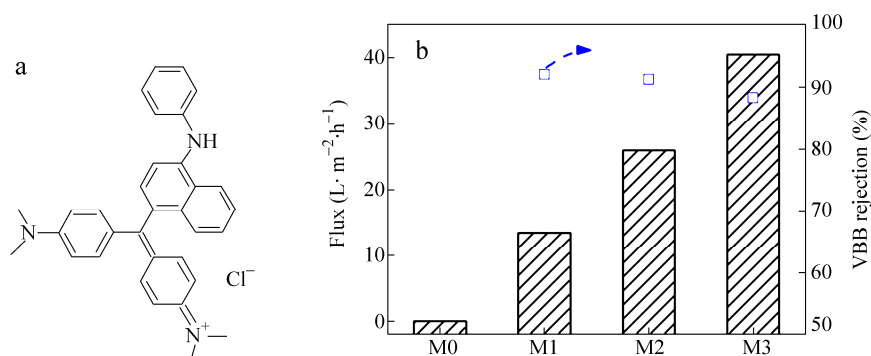


Fig. 9 (a) The structure of victoria blue B (VBB), (b) water fluxes and VBB rejections of PVC (M0) and copolymer membranes (M1, M2 and M3)

The separation performances of the membranes can be primarily determined by dye solution filtration experiments. Considering that the membranes are endowed with positive charges on their surface, VBB (Fig. 9a) was used as a model molecule for separation characterization in this study. The rejection test is carried out on Millipore UF stirred cell with high-speed stirring, which could avoid the concentration polarization effect as much as possible. As can be seen from Fig. 9(b), the rejections for M1, M2 and M3 are 92.0%, 91.2% and 88.2%, respectively, and M1 and M2 present the higher VBB rejection than M3. The reason lies on the PDMA content in the copolymer. PDMA chains in the copolymer membranes act not only as a type of hydrophilic additive, but also as a pore forming agent. They would improve the hydrophilicity of the membrane as well as enlarge the pore size/porosity of membrane. So that the membrane with suitable PDMA content in the copolymer would improve its permeability without reducing separation performance, which is mainly ascribed to promote the wettability and interconnectivity of the membrane (*e.g.* M2). But for the membranes with high PDMA content (*e.g.* M3), the pore size on the top layer would be increased gradually which would result in the higher flux but a lower rejection. Fan *et al.*^[44] have also observed that with the addition of polyvinyl formal (PVF) during PVC ultrafiltration, the flux of PVC membranes increased and the rejection decreased. They have proven that the hydrophilic PVF acted as pore forming agent during the NIPS process. Here the grafted PDMA chains does the similar function as that of PVF. So PDMA% in the copolymer should be optimized for the best filtration performances of the copolymer membranes. As is observed from experiments, the membranes with 31.1% PDMA chains show a better permeability and separation performance.

Phase separation method has been taken as an effective method for preparing nanofiltration membranes. For this purpose, one of the most interesting materials, cellulose acetate (CA)^[45, 46] is used with regard to its low cost and its chlorine resistance. Mayes *et al.*^[19] have reported an antifouling and high flux nanofiltration membrane prepared from polyacrylonitrile-*g*-poly(ethylene oxide) *via* coating and phase separation process. Also the membrane is proven to retain brilliant blue R (1.11 nm in size) and congo red (1.01 nm in size), as well as its water flux is $(85 \pm 25) \text{ L} \cdot \text{m}^{-2} \cdot \text{h}^{-1} \cdot \text{MPa}^{-1}$. The membrane is endowed with negative charges, which is beneficial for negative dye separation. While the membranes in this work are positively charged and so are better for positive dye separation.

The permeation and separation ability of the membranes in this work are comparable to those of Mayes's work^[19]. Compared to the traditional method for the preparation of nanofiltration membranes including interfacial polymerization and UV-induced grafting, the nanofiltration membranes here are prepared by one-step phase separation process, which is a relatively facile way. Despite few disadvantages for this membrane for nanofiltration such as the thick separation layer, being about 0.1–1.0 μm and lack of rigid supporting layer, this work still implies the potential of PVC-*g*-PDMA copolymers for nanofiltration. The work for membranes with thin supporting layer aiming for the better permeation and separation performances is still on the way. Moreover, PVC-*g*-PDMA could act not only as a kind of improved membrane material, but also as an additive to blend with

PVC membranes to achieve high performances. Since the tertiary amine groups in the PDMA chains are introduced into the novel polymer, such blend membranes could be modified further, including zwitterionization and quaterization. The former could improve the hydrophilicity, anti-fouling properties and biocompatibility of the membranes, while the latter would favor the antibacterial and special filtration properties due to the positive charges present in them.

CONCLUSIONS

The PVC-g-PDMA copolymer was successfully synthesized by ATRP process utilizing the labile chlorines on PVC backbones. The polymerization is proven to be controllable at a low conversion rate. Based on the synthesized copolymer, a new type of hydrophilic nanofiltration membrane was prepared by NIPS process. The copolymer membranes are found to be more hydrophilic and positively charged compared to the pure PVC one. When PDMA% is about 31.1%, the membrane showed a better permeability and VBB rejection. The copolymer, PVC-g-PDMA is primarily proven for nanofiltration membrane. Furthermore, since the tertiary amine group could be easily zwitterionized and quaterized, PVC-g-PDMA can also be used as a potential additive for PVC membranes that are used in the field of water treatment to improve the fouling resistance and antibacterial property.

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