Poly(vinylidene fluoride) with Grafted Poly(ethylene glycol) Side Chains via the RAFT-Mediated Process and Pore Size Control of the Copolymer Membranes

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ABSTRACT: Preparation of graft copolymers via living radical graft polymerization of poly(ethylene glycol) methyl ether methacrylate (PEGMA) with poly(vinylidene fluoride) (PVDF) in the reversible addition−fragmentation chain transfer (RAFT)-mediated process was carried out. The peroxides generated on the ozone-pretreated PVDF facilitated the thermally initiated graft copolymerization of PEGMA in the RAFT-mediated process. The chemical composition and structure of the copolymers were characterized by nuclear magnetic resonance (NMR), Fourier transform infrared (FTIR) spectroscopy, and molecular weight measurements. The "living" character of the grafted PEGMA side chains was ascertained in the subsequent block copolymerization of styrene. Microfiltration (MF) membranes were fabricated from the PVDF-*g*-PEGMA comb copolymers by phase inversion in aqueous media. Surface composition analysis of the membranes by X-ray photoelectron spectroscopy (XPS) revealed a substantial surface enrichment of the PEGMA graft chains. The pore size distribution of the resulting membranes was found to be much more uniform than that of the corresponding membranes cast from PVDF-*g*-PEGMA prepared by the conventional radical polymerization process in the absence of the chain transfer agent. The morphology of the membranes was characterized by scanning electron microscopy. The pore size and distribution varied with the graft concentration and the density of graft points. The PVDF-*g*-PEGMA MF membranes displayed substantial resistance to γ-globulin fouling, in comparison to the pristine hydrophobic PVDF MF membranes.

Introduction

Graft copolymerization of a functional monomer with an existing polymer offers an effective approach to incorporating new properties into the parent polymer, while retaining the desirable properties of the parent polymer.[1−3] Compared to the parent polymers, graft copolymers often exhibit improved physicochemical properties, such as enhanced compatibility with other polymers, adhesion to metallic and inorganic substrates, and dye retention.[4] In particular, the grafting of hydrophilic species onto hydrophobic polymers is of great utility. Amphiphilic graft copolymers so prepared often display enhanced surface properties, such as improved resistance to the adsorption of oils and proteins, biocompatibility, and reduced static charge buildup. Because of their potential applications, methods for preparing graft copolymers from poly(vinylidene fluoride) (PVDF) have received considerable attention.[5−8] For example, polyelectrolytes based on amphiphilic graft copolymers of PVDF incorporating poly(ethylene glycol) monomethacrylate chains have been prepared.[6]

The synthesis of graft copolymers based on commercial polymers is most commonly accomplished via the free-radical process. Free radicals are produced on the parent polymer chains by exposure to ionizing radiation and/or a free-radical initiator.[1,4,9] Alternatively, peroxide groups are introduced onto the parent polymer by ozone pretreatment to serve as the initiation sites for the free-radical polymerization of a monomer.[5,6,10−13]

Progress in polymer synthesis techniques makes it possible to produce well-defined graft polymer chains (polymer brushes) with controlled lengths and specific chain architectures. Atom transfer radical polymerization (ATRP) has been used to prepare graft copolymers from polymeric macroinitiators—polymer chains with regularly spaced pendant chemical groups containing radically transferable halogen atoms.[14] ATRP of the poly(ethylene glycol) methyl ether methacrylate (PEGMA) macromonomer, having roughly nine ethylene oxide (EO) units, has been carried out to prepare the amphiphilic graft copolymer with PVDF.[15] Reversible addition−fragmentation chain transfer (RAFT)-mediated polymerization is an alternative method for achieving controlled free radical polymerization in solution.[16−23] It involves a reversible addition−fragmentation cycle, in which transfer of a dithioester moiety between the active and dormant species maintains the controlled character of the polymerization process.

On the other hand, the PVDF membranes are widely used in microfiltration (MF) and ultrafiltration (UF) due to their excellent processability, chemical resistance, well-controlled porosity, and good thermal property.[24] Several approaches have been developed to endow the conventional hydrophobic membranes with hydrophilic properties. These approaches have included coating and grafting techniques. In the former approach, the membranes are dipped in solutions containing the hydrophilic polymers.[25,26] The approach of molecular or bulk graft copolymerization of a functional (hydrophilic) monomer with a hydrophobic polymer, followed by phase inversion in an aqueous medium, to membrane fabrication may prove to be particularly useful in certain cases.[27−29] Graft copolymerization via the conventional free-radical process usually leads to uncontrolled size distribution of the graft chains. Graft copolymerization by the RAFT-mediated process, however, can be ex-

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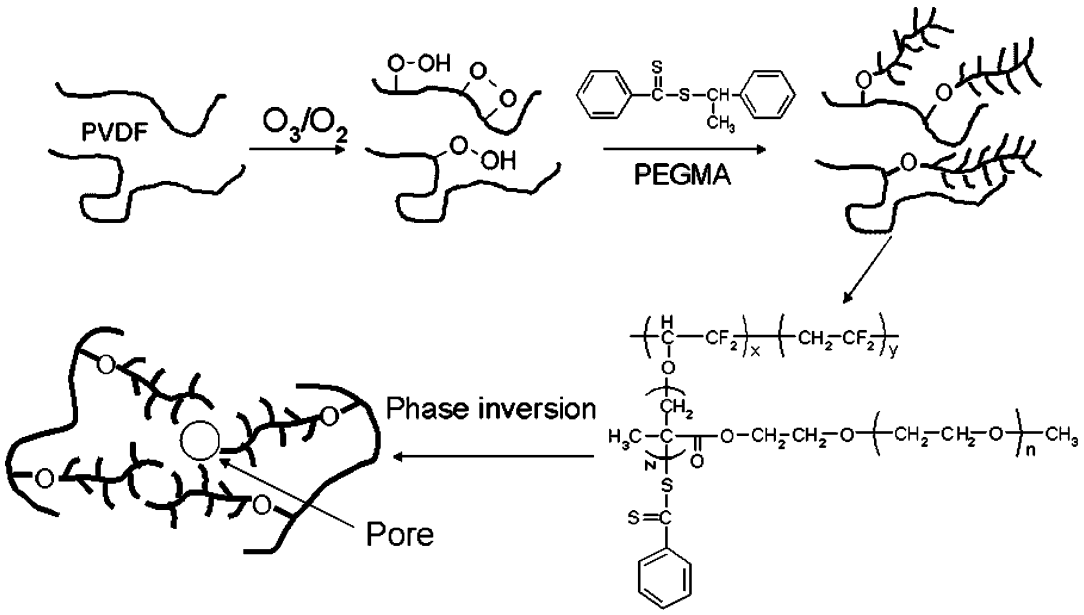
Scheme 1. Schematic Illustration of the Processes of PEGMA Graft Copolymerization with the Ozone-Preactivated PVDF Backbone by RAFT-Mediated Polymerization and the Preparation of the PVDF-*g*-PEGMA MF Membrane by Phase Inversion



pected to produce well-defined side chains, which, in turn, can be expected to improve the uniformity in pore size distribution of the membrane during the phase inversion process.

Experimental Section

Materials. Poly(vinylidene fluoride) (Kynar K-761) powders having a molecular weight of 441 000 were obtained from Elf Atochem of North America Inc. The monomer poly(ethylene glycol) methyl ether methacrylate ($\overline{M}_n$ = 300 g/mol) was purchased from Aldrich Chemical Co. (Milwaukee, WI) and was used after removal of the inhibitor in an Al_2O_3 column. The solvent, *N*,*N*-dimethylformamide (DMF), was purchased from Fisher Scientific Co., Leics, UK, and was used as received. The chain transfer agent (CTA), 1-phenylethyl dithiobenzoate (PDB), was prepared according to the published procedures.[15,16] The protein, γ-globulin, was obtained from the Sigma Chemical Co. of St. Louis, MO.

RAFT-Mediated Graft Copolymerization of PEGMA with PVDF (PVDF-*g*-PEGMA). The PVDF powders were dissolved in DMF to a concentration of 75 g/L. A continuous stream of O_3/O_2 mixture was bubbled through 27 mL of the solution at 25 °C. The O_3/O_2 mixture was generated from an Azcozon RMU 16-04EM ozone generator. The gas flow rate was adjusted to 300 L/h to give rise to an ozone concentration of about 0.027 g/L of the gaseous mixture. A typical treatment time of about 15 min was used. This pretreatment time gave rise to a peroxide content of about 10^{-4} mol/g of the polymer.[30] The ozone treatment time was also varied to change the density of graft points (initiation sites) on the PVDF chains. The dependence of peroxide concentration and molecular weight of PVDF on the ozone treatment time under similar experimental conditions had been reported earlier.[30] The ozone-pretreated PVDF solution (containing about 2 g of PVDF) and 2 mL of the DMF solution of PDB (1.46×10^{-1} mol/L) were transferred to an ampule. DMF solution of PEGMA was then introduced into the ampule to give a final volume of 60 mL and a PEGMA concentration ranging from 0.08 to 0.31 g/mL. The ampules were degassed with three freeze−evacuate−thaw cycles. They were then sealed and heated at 60 °C for 6 h. After the desired reaction time, the reactor flasks were cooled in an ice bath. The PVDF-*g*-PEGMA copolymers were precipitated from a mixture of 1 part ethanol and 1−2 parts petroleum ether and recovered by filtration. Since ethanol is a good solvent for the PEGMA homopolymer, the homopolymer of PEGMA generated during the RAFT-mediated graft copolymerization process should have been extracted out. The copolymers were purified thrice by redissolving in DMF and reprecipitating in an ethanol/petroleum ether mixture. The graft copolymers were further purified by extracting with ethanol for 48 h in order to remove the residual homopolymer of PEGMA, if any. Finally, the copolymers were dried by pumping under reduced pressure overnight at room temperature.

Preparation of the MF Membranes. Each microfiltration (MF) membrane was prepared by phase inversion in an aqueous medium from a 12 wt % DMF solution of the copolymer. The copolymer solution was cast onto a glass plate, which was then immersed in a bath of doubly distilled water (nonsolvent) after the polymer solution had been subjected to a brief period of evaporation in air. The temperature of the water in the casting bath was controlled at 22 °C. Each membrane was left in water for about 20 min after separation from the glass plate. It was then extracted in a second bath of double-distilled water at 70 °C for 15 min. Such a heat treatment step was commonly performed during the fabrication of commercial membranes in order to refine the pore size distribution.[31] The purified membranes were dried by pumping under reduced pressure for subsequent characterization. The processes for the RAFT-mediated synthesis of the PVDF-*g*-PEGMA copolymer and the preparation of the MF membrane are illustrated in Scheme 1.

Characterization of the Graft Copolymers. Fourier transform infrared (FTIR) spectra of the graft copolymers were recorded on a Bio-Rad FTS 135 FTIR spectrophotometer, with the copolymer samples dispersed in KBr pellets. Each spectrum was collected by cumulating 16 scans at a resolution of 8 cm^{-1}. Proton nuclear magnetic resonance (^{1}H NMR) was performed on a Bruker ARX 300 instrument with deuterated DMF as the solvent. Gel permeation chromatography (GPC) was performed using DMF as the eluent and polystyrene standards as the references. The thermal properties of the copolymers were measured by thermogravimetric analyses (TGA). The samples were heated to 700 °C at a heating rate of 20 °C/min under a dry nitrogen atmosphere in a Du Pont Thermal Analyst 2100 system equipped with a TGA 2050 thermogravimetric thermal analyzer. X-ray photoelectron spectroscopy (XPS) measurements were made on a Kratos AXIS HSi spectrometer with a monochromatized Al Kα X-ray source (1486.7 eV photons) at a constant dwelling time of 100 ms and a pass energy of 40 eV. The anode current was 15 mA.

The pressure in the analysis chamber was maintained at 5×10^{-8} Torr or lower during each measurement. The membranes were mounted on the standard sample studs by means of double-sided adhesive tapes. The core-level signals were obtained at the photoelectron takeoff angle (α, with respect to the sample surface) of 90°. Surface elemental stoichiometries were determined from peak area ratios, after correcting with the experimentally determined sensitivity factors, and with reliable to ±5%. The surface morphology of the MF membranes was studied by scanning electron microscopy (SEM), using a JEOL 6320 electron microscope. The membranes were mounted on the sample studs by means of double-sided adhesive tapes. A thin layer of platinum was sputtered on the sample surface prior to the SEM measurement. The SEM measurements were performed at an accelerating voltage of 15 kV. The pore sizes of the MF membranes were measured using a Coulter Porometer II apparatus of the Coulter Electronics Ltd., Luton, UK. POROFIL (the pore-wetting liquid for the Coulter Porometer apparatus) was used as the wetting agent. The morphology of the PVDF-*g*-PEGMA copolymer in the neat state was characterized by transmission electron microscopy (TEM). Thin film specimens for TEM measurements were prepared via solution casting at room temperature. About 1 μL of the 0.01 wt % DMF solution of PVDF-*g*-PEGMA was first introduced onto a 400 mesh copper TEM grid (Ted Pella Inc.) and then dried for several days inside an isolated DMF atmosphere. The film was exposed for a few hours in air before being finally pumped for an hour under reduced pressure. This procedure resulted in the formation of a copolymer film of approximately 50−100 nm in thickness, freely extended across the metal grid. The sample film mounted on the grid was stained with osmium tetraoxide for 10 min at room temperature. TEM measurements were performed on a JEOL 2010 microscope operating in the bright field mode and with an accelerating voltage of 200 kV. Static water contact angles of the graft copolymer films cast by spin-coating were measured at 25 °C and 60% relative humidity on a telescopic goniometer (Rame-Hart, model 100-00(230)). The telescope with a magnification power of 23× was equipped with a protractor of 1° graduation. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to ±3°.

Protein Fouling Measurements. To investigate the antifouling properties of the PVDF-*g*-PEGMA membranes, the membranes were first exposed to solutions containing γ-globulin. The membranes were hydrated initially by immersion in methanol, followed by immersion in distilled water. The membranes were subsequently washed with the phosphate−buffer saline (0.01 M PBS, pH 7.4) for 1 h before being incubated in PBS containing 2 mg/mL of γ-globulin for 24 h at room temperature. After removal from the protein solution, they were washed for 5 min in three batches of PBS, followed by three batches of distilled water. Finally, samples were dried in a vacuum oven at room temperature. The surface coverage of γ-globulin was quantified by XPS, using the nitrogen signal associated with γ-globulin. Survey spectra were run in the binding energy range of 0−1000 eV. The near-surface atomic compositions of the membranes were determined from the numerically integrated core-level spectral area ratios, corrected with the respective elemental sensitivity factors. Permeation experiments were performed at room temperature (25 °C) and 8 kPa transmembrane pressure using a stirred microfiltration cell (Toyo Roshi UHP-25, Tokyo, Japan). The concentration of the protein (γ-globulin) solution (PBS, pH 7.4) was 1 mg/mL. The effective membrane area was 3.14 cm^2. The flux was calculated from the weight of the solution permeated per unit time and per unit area of the membrane surface.

Results and Discussion

Chemical Structure of the Graft Copolymers. The chemical structure of the graft copolymer PVDF-*g*-PEGMA was first characterized by ^{1}H NMR spectroscopy. The chemical shifts at 2.9 and 2.4 ppm are attributable to the CH_2 of PVDF, arising from the well-known head-to-tail (ht) and head-to-head (hh) bonding arrangements, respectively.[32] Grafting of the PEGMA polymer to PVDF has resulted in the appearance of chemical shifts at 3.2 ppm, in the region of 3.5−3.7 ppm, at 4.2 ppm, and in the region of 0.9−1.9 ppm, attributable respectively to the OCH_3 terminal group, the OCH_2 group, the COOCH_2 group, and the backbone hydrogen species of the grafted PEGMA chain. The molar ratio of the PEGMA units in the graft chains relative to the number of repeating units of PVDF in the copolymer was then calculated on the basis of the ratio of the integrals of the resonance at 4.2 ppm to that of the combined resonances at 2.9 and 2.4 ppm. The graft composition so calculated is shown in Table 1. The dithiobenzoate end group of the graft chain, which is associated with the chain transfer agent, was discernible in the region of 7.5−7.9 ppm in the spectrum.[16] The presence of the dithiobenzoate end group confirmed that the graft copolymerization had proceeded via the RAFT-mediated process. The ^{1}H NMR spectrum of the PVDF-*g*-PEGMA copolymer with a $([-\text{PEGMA}-]/[-CH_2CF_2-])_{bulk}$ ratio of 0.08 is shown in Figure 1. The solvent peaks s_2 and s_3 were subtracted from the spectrum using their known intensities relative to that of the solvent peak s_1, obtained from the analysis of pure deuterated DMF.

Table 1. Experimental Parameters and Chemical Composition of the PVDF-*g*-PEGMA

polymer	peroxides content,[a] mol/g of PVDF	[−PEGMA−]/[−CH_2CF_2−] or [PEGMA]/[−CH_2CF_2−] feed molar ratio[e]	graft molar ratio (bulk)	weight loss,[b] wt %
PVDF		0	0	0
conv[c]	10×10^{-5}	1.1	0.06	22
a	10×10^{-5}	0.5	0.02	8.6
b	10×10^{-5}	0.8	0.04	17
c	10×10^{-5}	1.1	0.08	26
d	10×10^{-5}	1.5	0.09	30
e	10×10^{-5}	2.0	0.13	38
$c_{5\ min}$[d]	5×10^{-5}	1.1	0.03	11
$c_{10\ min}$	8×10^{-5}	1.1	0.04	17
$c_{15\ min}$	10×10^{-5}	1.1	0.08	26

[a] Determined from the reaction with DPPH. The ozone pretreatment time for samples a−e was 15 min. [b] The extent of the first major loss in the TGA under a nitrogen atmosphere. [c] PVDF-*g*-PEGMA prepared by heating PEGMA (0.573 M) and 15 min ozone-preactivated PVDF (0.0333 g/mL) at 60 °C in DMF for 6 h in the absence of PDB. [d] The subscript denotes the ozone pretreatment time of PVDF. [e] Based a [−CH_2CH_2−] concentration of 0.52 mol/L and a chain transfer agent (PDB) concentration of 4.87×10^{-3} mol/L.

The chemical structures of the graft copolymers were also studied by FTIR spectroscopy. The absorption band at 1730 cm^{-1}, associated with C═O stretching of the PEGMA polymer chains, is present in all the PVDF-*g*-PEGMA samples. On the other hand, the absorption band in the region of 1120−1280 cm^{-1}, characteristic of the CF_2 functional groups of PVDF, is also present in all the copolymer samples. With the increase in [PEGMA] to [−CH_2CF_2−] molar feed ratio, the intensity of the absorption band at 1730 cm^{-1} is enhanced, consistent with an increase in concentration of the grafted PEGMA polymer side chains.

Molecular Weight of the PVDF-*g*-PEGMA Copolymer. The molecular weight and polydispersity of the graft copolymers, obtained from the GPC traces, are presented in Table 2. Grafting of the PEGMA polymer to PVDF has resulted in a significant increase in molecular weight relative to the PVDF parent polymer.

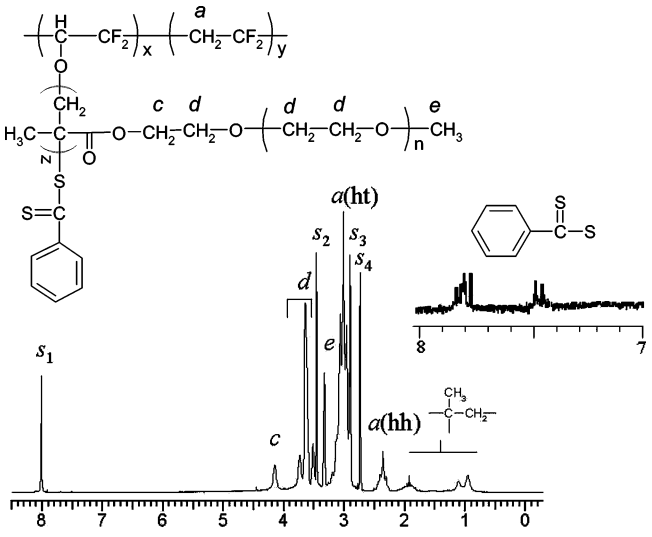


Figure 1. The 300 MHz ^{1}H NMR spectra of the PVDF-*g*-PEGMA copolymer with a $([-\text{PEGMA}-]/[-CH_2CF_2-])_{bulk}$ ratio of 0.08. Resonances labeled s_n are solvent peaks due to deuterated DMF.

The molecular weight distribution (MWD) of the PVDF-*g*-PEGMA copolymers was unimodal. The MWDs of the graft copolymers obtained from GPC appeared to be narrower than that of the PVDF base polymer. This observation is not expected, as the MWD of a graft copolymer should not be narrower than that of the base polymer. The observed decrease in polydispersity of the graft copolymer is most likely to have resulted from preferential removal of the low molecular weight fraction of the copolymer during the repeated precipitation and extraction process employed to purify the copolymer after the RAFT-mediated graft copolymerization process. It should also be noted that molecular weight determinations of the PVDF-*g*-PEGMA copolymers using polystyrene standards would only provide a general indication on the changes in molecular weight and MWD. The remote resemblance in structure between polystyrene and the PVDF-*g*-PEGMA copolymer, as well as the expected changes in hydrodynamic volume when the hydrophobic PVDF is grafted with increasing amount of the hydrophilic PEGMA polymer, may significantly affect the molecular weight determination.

The number-averaged molecular weights were also obtained from the NMR results using the relationship $M_{n,graft} = M_{n,PVDF}[1 + x(M_{0,PEGMA}/M_{0,PVDF})]$, where $M_{n,PVDF}$ is the number-averaged molecular weight of the parent PVDF obtained from GPC measurement, x is the molar ratio of the PEGMA units per PVDF repeat unit in the copolymer as measured by NMR, and $M_{0,PVDF}$ and $M_{0,PEGMA}$ are the molar masses of the PVDF repeat unit and of PEGMA, respectively. The values of M_n of the graft copolymers so calculated are also shown in Table 2 for comparison purpose. The averaged molecular weight of the graft chains was estimated from the peroxide concentration of the ozone-preactivated PVDF and the graft concentration. The M_n of the graft chains ranges from 900 to 6100 (Table 2). Ideally, the proportion of the PEGMA graft chains in the RAFT-mediated process (Table 1) should resemble that of the corresponding PEGMA homopolymer in the reaction mixture. Attempts to recover the PEGMA homopolymer from the reaction mixture were not successful because of the good solubility of the PEGMA polymer in organic and aqueous solvents as well as the presence of unreacted PEGMA monomer in the reaction mixture.

Poly(vinylidene fluoride)-*graft*-Poly(ethylene glycol) Methyl Ether Methacrylate-*block*-Polystyrene. To further ascertain the presence of a RAFT-mediated process during graft copolymerization, the PVDF-*g*-PEGMA copolymer was subsequently block copolymerized with styrene. PVDF-*g*-PEGMA ($([-\text{PEGMA}-]/[-CH_2CF_2-])_{bulk} = 0.02$, 0.2 g, $M_n = 223\,300$, $M_w/M_n = 1.71$, prepared as described above), styrene (2 mL), 2,2′-azobis(isobutyronitrile) (AIBN, 0.5 mg), PDB (0.6 mg), and DMF (8 mL) were transferred into an ampule. The resulting mixture was degassed, sealed, and heated at 60 °C for 12 h. The resulting copolymer was precipitated in ethanol and extracted vigorously with toluene to remove the styrene homopolymer (PS). The volatiles were removed in vacuo to give rise to a PVDF-*g*-PEGMA-*b*-PS with $M_n = 315\,300$ and $M_w/M_n = 1.56$. The absorption bands at 1600 and 1500 cm^{-1}, attributed to the benzene ring of styrene, are observable in the FTIR spectrum of the block graft copolymer. No absorption bands characteristic of styrene, however, could be found in the FTIR spectrum of the corresponding blend of PVDF-*g*-PEGMA with PS after the similar extracting process in toluene.

Thermogravimetric Analysis of the Graft Copolymers. A distinct two-step degradation process was observed for the copolymer samples during thermogravimetric analyses. The onset of the first major weight loss at about 250 °C corresponds to the decomposition of the grafted PEGMA polymer component. The second major weight loss begins at about 470 °C, corresponding to the commencement of the decomposition of the PVDF chain.[33] The extent of the first major weight loss, shown in Table 1, coincides approximately with the bulk PEGMA content in the respective graft copolymer, as

Table 2. Molecular Weights of the PVDF Base Polymer and Graft Copolymers

polymer	$[\text{PEGMA}]/[-CH_2CF_2-]$ molar feed ratio	GPC molar mass (g/mol)[a] $\overline{M_n}$	GPC molar mass (g/mol)[a] $\overline{M_w}/\overline{M_n}$	est molar mass $\overline{M_n}$[b]	graft chain $\overline{M_n}$[c]
PVDF	0	194 000	1.84	194 000[a]	0
conv[d]	1.1	332 700	1.93	248 500	2800
a	0.5	223 300	1.71	212 200	900
b	0.8	264 100	1.69	230 400	1800
c	1.1	367 300	1.36	266 700	3700
d	1.5	379 400	1.42	275 800	4200
e	2.0	405 600	1.33	312 200	6100
$c_{5\ min}$	1.1	257 700	1.62	221 300	2800
$c_{10\ min}$	1.1	270 400	1.58	230 400	2600

[a] From GPC measurements, based on polystyrene standards. [b] Estimated from the ^{1}H NMR derived composition. [c] The average molecular weight of the graft chains was calculated from the peroxide concentration of the ozone-preactivated PVDF and the graft concentration. [d] From conventional free-radical-initiated graft copolymerization in the absence of the chain transfer agent. [e] For samples a−e, the ozone-pretreatment time for PVDF was fixed at 15 min.

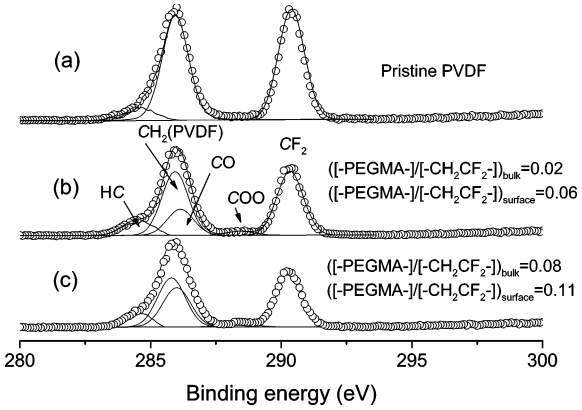


Figure 2. C 1s core-level spectra for membranes cast by phase inversion from 12 wt % DMF solutions of (a) the pristine PVDF and the PVDF-*g*-PEGMA copolymers having $([-\text{PEGMA}-]/[-\text{CH}_2\text{CF}_2-])_{\text{bulk}}$ ratio of (b) 0.02 and (c) 0.08.

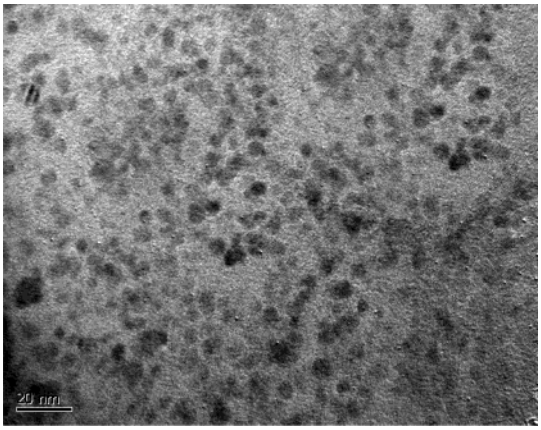


Figure 3. TEM micrograph of a PVDF-*g*-PEGMA film stained with osmium tetraoxide. The stained PEGMA nanodomains appear as darker regions in the image.

calculated from the NMR data and converted to the mass basis.

Surface Compositions of the PVDF-*g*-PEGMA Membranes. The near-surface compositions of the PVDF-*g*-PEGMA membranes are determined from the curve-fitted C 1s core-level spectra. Figure 2 shows the curve-fitted C 1s core-level spectra of the PVDF membrane and two graft copolymer membranes with bulk graft concentrations of 0.02 and 0.08 cast by phase inversion from the respective 12 wt % DMF solutions. Two peak components of about equal intensities (with BE at 286.2 eV for the CH_2 species and at 290.7 eV for the CF_2 species) can be assigned to the PVDF main chains. The components with BE at 284.6, 286.4, and 288.7 eV are attributed to the *C*H, *C*−O, and *C*OO species, respectively, of the grafted PEGMA chain. From the curve-fitted C 1s core-level spectra, the near-surface mole ratio of PEGMA was calculated as $([-\text{PEGMA}-]/[-\text{CH}_2\text{CF}_2-])_{\text{surface}} = A_{\text{COO}}/A_{\text{CF}_2}$, where A_{COO} and A_{CF_2} are the areas of the *C*OO and CF_2 peak components, respectively. The near-surface PEGMA polymer concentration for each copolymer sample is given in Table 3 and is always much higher than the corresponding bulk concentration. Obviously, significant surface aggregation of the hydrophilic graft chains has occurred during membrane fabrication by phase inversion in an aqueous medium because of the relatively low interfacial energy between the PEGMA graft chain and water.[34]

A substantial decrease in water contact angle of the PVDF film can be achieved through graft copolymerization with PEGMA. A static water contact angle as low as 16° was obtained at the surface graft concentration of about 0.24. The phenomenon is attributed to the hydrophilic nature of the grafted PEGMA side chains and their aggregation in the surface region. The water contact angles for the PVDF-*g*-PEGMA copolymers of various graft concentrations are summarized in Table 3. Thus, with the increase in the PEGMA graft concentration, the surface water contact angle of the copolymer film decreases.

Morphology and Architecture. Figure 3 is a TEM micrograph of the PVDF-*g*-PEGMA film $(([-\text{PEGMA}-]/[-\text{CH}_2\text{CF}_2-])_{\text{bulk}} = 0.08)$ stained with osmium tetraoxide. The latter selectively stains the ether oxygen moieties in PEGMA and is incorporated into the copolymer.[35] The TEM image reveals an apparently nanophase-segregated structure, as indicated by the dark/stained PEGMA domains. The morphology of the PVDF-*g*-PEGMA MF membranes was studied by SEM. The SEM images in Figure 4 are obtained at a magnification of 10 000× for MF membranes cast by the phase inversion at 22 °C in water from 12 wt % DMF

Table 3. Characteristics of the PVDF-*g*-PEGMA MF Membranes

membrane[a]	[−PEGMA−]/[−CH_2CF_2−] or [PEGMA]/[−CH_2CF_2−] feed ratio	graft ratio (bulk)	graft ratio (surface)	contact angle[c] (deg)	pore size max[b] (μm)	pore size min[b] (μm)	pore size mean[b] (μm)	pore density[b] × 10^9/cm^2
PVDF	0	0	0	124				
conv[d]	1.1	0.06	0.09	28	2.56	0.52	1.61	1.24
(A) Influence of Graft Concentration on the Pore Size of the Membranes								
a	0.5	0.02	0.06	34	0.72	0.29	0.50	11.1
b	0.8	0.04	0.09	30	0.98	0.34	0.67	8.20
c	1.1	0.08	0.11	21	1.53	0.66	0.83	4.27
d	1.5	0.09	0.12	19	1.82	0.56	1.01	1.93
e	2.0	0.13	0.24	16	1.83	0.71	1.24	1.87
(B) Influence of Graft Points (Initiation Sites) on the Pore Size of the Membranes								
$c_{5\ \text{min}}$[e]	1.1	0.03	0.07	35	2.12	0.48	1.67	1.85
$c_{10\ \text{min}}$	1.1	0.04	0.08	32	1.75	0.43	1.45	2.29
$c_{15\ \text{min}}$	1.1	0.08	0.11	21	1.53	0.66	0.83	4.27

[a] Microfiltration membranes (thickness 390 μm) cast from 12 wt % of the PVDF-*g*-PEGMA in DMF solution at 22 °C by phase inversion. [b] Pore sizes were measured on the Coulter Porometer II which utilized a liquid displacement technique. [c] The films for static water contact angle measurements were cast from DMF solution of the pristine PVDF and the PVDF-*g*-PEGMA copolymers. [d] PVDF-*g*-PEGMA prepared by heating PEGMA (0.573 M) and 15 min ozone-preactivated PVDF (0.0333 g/mL) at 60 °C in DMF for 6 h in the absence of PDB. [e] The subscript denotes the ozone pretreatment time of PVDF.

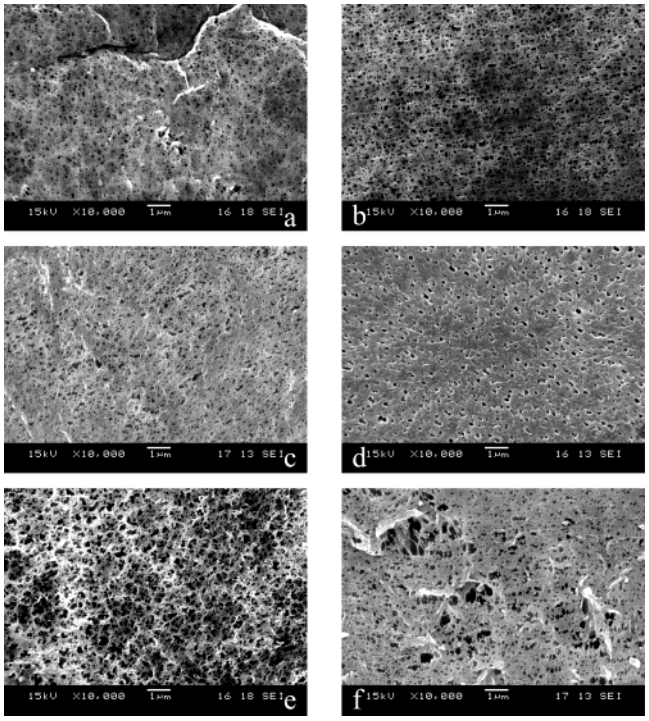


Figure 4. SEM micrographs of the MF membranes cast at 22 °C by phase inversion from 12 wt % DMF solutions of the PVDF-*g*-PEGMA copolymers with graft concentrations ([−PEGMA−]/[$-CH_2CF_2-$] bulk ratios) of (a) 0.02, (b) 0.04, (c) 0.08, (d) 0.09, and (e) 0.13 prepared in the presence of PDB and (f) 0.06 prepared in the absence of PDB.

solutions of five PVDF-*g*-PEGMA copolymers of different graft concentrations. The SEM image of the MF membrane prepared from the PVDF-*g*-PEGMA copolymer synthesized by the conventional free-radical polymerization technique (in the absence of the chain transfer agent PDB) is also included for comparison purpose. A much more uniform pore size distribution is observed for the membranes from copolymers prepared by the RAFT-mediated process. The higher the graft concentration of the PEGMA chains in the copolymer, the larger the pore size and the less uniform the pore size distribution. The dependence of the membrane morphology on the density of grafting points (initiation sites, dictated by the ozone pretreatment time) is also investigated. The SEM images, obtained at a magnification of 30 000×, for MF membranes prepared from graft copolymers with varying ozone pretreatment time, while fixing the molar feed ratio of PEGMA to PVDF at 1.1, are shown in Figure 5. With decreasing ozone pretreatment time to 10 and 5 min from 15 min, the pore size of the corresponding MF membranes increases and the pore size distribution becomes less uniform. On the other hand, no pores were discernible from SEM image of the PVDF membrane prepared by the same way.

Pore Size of the PVDF-*g*-PEGMA Membranes. The pore size and pore size distribution of the various PVDF-*g*-PEGMA membranes, as measured on the Coulter Porometer II apparatus, are summarized in Table 3. The "POROFIL"[36] wetted sample is subjected to an increasing pressure, exerted by a gas source. As the pressure of the gas increases, it will reach a point at which it can overcome the surface tension of the liquid in the largest pores and will push the liquid out. The pressure is termed the minimum bubble point and corresponds to the measurement of maximum pore size. Increasing the pressure still further allows the gas to

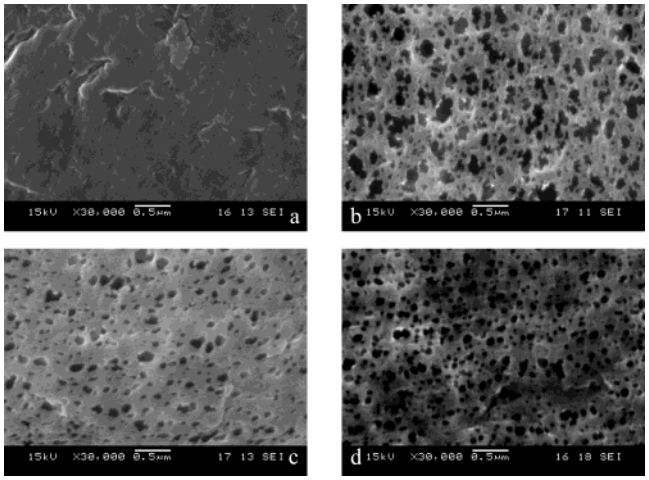


Figure 5. SEM micrographs of the MF membranes cast by phase inversion from 12 wt % DMF solutions of (a) the pristine PVDF and the PVDF-*g*-PEGMA copolymers prepared by the RAFT-mediated process with PVDF having ozone pretreatment time of (b) 5, (c) 10, and (d) 15 min. The three PVDF-*g*-PEGMA copolymers correspond to samples c_{5min}, c_{10min}, and c_{15min} in Table 1.

flow through smaller pores, until all of the pores have been emptied. The result is governed by the Washburn equation:[37] $Pr = 2\gamma \cos \theta$, where P is the pressure, r the average pore radius of a membrane, and $\gamma \cos \theta$ the Wilhelmy surface tension. The data in Table 3 show that the pore size distribution of the PVDF-*g*-PEGMA membranes prepared by the RAFT-mediated process is much more uniform than that prepared by conventional free-radical polymerization. With the increase in graft concentration or lowering of the ozone pretreatment time of PVDF, the variation in pore size and its distribution follow the same trend as that revealed by the SEM images. A promising MF membrane appears to be that with a maximum pore size of 0.72 μm and a minimum pore size of 0.29 μm, prepared from a molar feed ratio ([PEGMA]/[$-CH_2CF_2-$] ratio) of 0.5 by the RAFT-mediated process.

Antifouling Property of the PVDF-*g*-PEGMA MF Membranes. The presence of PEGMA chains on the membrane surface, including the pore surface, imparts significant resistance to protein adsorption. The surface composition of the membranes after exposure to a 2 mg/mL γ-globulin solution for 24 h was analyzed by XPS. The relative amount of γ-globulin adsorbed onto the surface can be simply expressed as the [N]/[F] ratio. The dependence of the [N]/[F] ratio on the PEGMA polymer graft concentration of the PVDF-*g*-PEGMA membrane is summarized in the inset in Figure 6. As in the cases of other membranes derived from or containing the PVDF-based amphiphilic comb polymers,[15,34,38−40] MF membranes of the PVDF-*g*-PEGMA copolymers show substantially enhanced resistance to γ-globulin adsorption, in comparison to pure PVDF membranes. The level of γ-globulin adsorption for the membrane with a bulk [−PEGMA−]/[$-CH_2CF_2-$] ratio of 0.02 is less than 15% of that of pristine PVDF membrane. For membranes with a bulk [−PEGMA−]/[$-CH_2CF_2-$] ratio of 0.13 and above, the amount of γ-globulin adsorption is negligible.

The protein (γ-globulin) solution flux data of Figure 6 allow a comparison of the antifouling property of the present PVDF-*g*-PEGMA membrane with the commercial PVDF membranes. Commercially hydrophilic and hydrophobic PVDF membranes of comparable pore

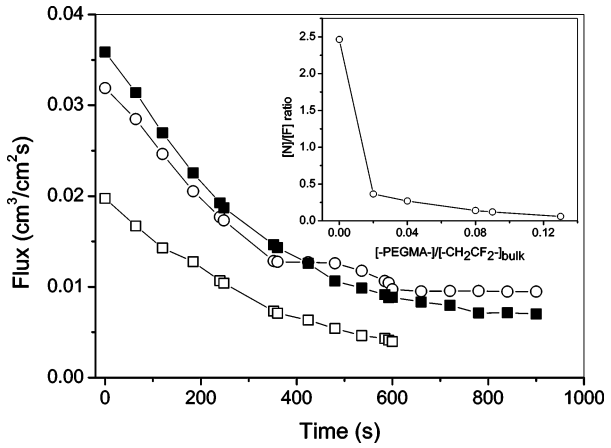


Figure 6. Decline in the permeation rate of the γ-globulin solution (1 mg/mL) as a function of time through the Millipore hydrophilic (solid square) and hydrophobic (open square) PVDF membranes (designation: $d = 0.22\ \mu$m, actual: maximum pore size = 0.79 μm, minimum pore size = 0.27 μm, and mean pore size = 0.57 μm) and the PVDF-*g*-PEGMA microporous membrane with a $([-\text{PEGMA}-]/[-CH_2CF_2-])_{bulk} = 0.02$ (open circle). Inset: the dependence of the extent of γ-globulin adsorption (expressed as the [N]/[F] ratio) on the PEGMA graft concentration in the PVDF-*g*-PEGMA membrane.

dimensions from Millipore were used in the permeation experiment. The flux of the protein solution through the PVDF-*g*-PEGMA microporous membrane with a bulk $[-\text{PEGMA}-]/[-CH_2CF_2-]$ ratio of 0.02, which has comparable mean pore size as that of the commercial membranes, shows an initial decrease. The flux eventually levels off at about half of the initial permeation rate. The PVDF-*g*-PEGMA membrane thus exhibits a better antifouling property in the dynamic fouling process than that of the pristine hydrophobic PVDF membrane. The antifouling ability of the PVDF-*g*-PEGMA membrane is comparable to that of the commercial "low-protein-binding" Millipore hydrophilic membrane. When subjected to prolonged flux, the present PVDF-*g*-PEGMA membrane exhibits even better fouling resistance than the commercial hydrophilic PVDF membrane. On the other hand, the flux of the protein solution through the commercial hydrophobic PVDF membrane became too low to be measured accurately after 600 s.

Conclusions

PVDF with living PEGMA side chains (PVDF-*g*-PEGMA) was successfully synthesized through molecular graft copolymerization of the PEGMA macromonomer with the ozone-preactivated PVDF backbone in the RAFT-mediated process. The MF membranes prepared from the amphiphilic PVDF-*g*-PEGMA copolymers of different graft concentration and of different graft chain density by phase inversion in an aqueous medium showed enrichment of the hydrophilic PEGMA polymer in the surface region. A much more uniform pore size distribution of the MF membranes was obtained, probably due to the presence of well-defined PEGMA side chains on the PVDF main chain arising from the RAFT-mediated process. The present study has shown that molecular functionalization by graft copolymerization using the RAFT-mediated technique is a promising approach to the preparation of membrane with uniform pore size distribution, refined pore size, and increased porosity. Protein adsorption and solution flux behavior through the copolymer membrane revealed that the PVDF-*g*-PEGMA MF membranes exhibited good antifouling properties.

References and Notes

(1) Uyama, Y.; Kato, K.; Ikada, Y. *Adv. Polym. Sci.* **1998**, *137*, 1.
(2) Battard, H. A. J.; Tregar, G. W. *Graft Copolymers*; Wiley-Interscience: New York, 1967.
(3) Ceresa, R. J. *Block and Graft Copolymerization*; Wiley-Interscience: New York, 1973; Vol. I.
(4) Xu, G. X.; Lin, S. G. *J. Macromol. Sci., Rev. Macromol. Chem. Phys.* **1994**, *C34*, 555.
(5) Boutevin, B.; Robin, J. J.; Serdani, A. *Eur. Polym. J.* **1992**, *28*, 1507.
(6) Liu, Y.; Lee, J. Y.; Kang, E. T.; Wang, P.; Tan, K. L. *React. Funct. Polym.* **2001**, *47*, 201.
(7) Mascia, L.; Hashim, K. *J. Appl. Polym. Sci.* **1997**, *66*, 1911.
(8) Valenza, A.; Carianni, G. *Polym. Eng. Sci.* **1998**, *38*, 452.
(9) Mukherjee, A. K.; Gupta, B. D. *J. Macromol. Sci., Chem.* **1983**, *A19*, 1069.
(10) Boutevin, B.; Robin, J. J.; Torres, N.; Casteil, J. *Polym. Eng. Sci.* **2002**, *42*, 78.
(11) Boutevin, B.; Robin, J. J.; Torres, N.; Casteil, J. *Macromol. Chem. Phys.* **2002**, *203*, 245.
(12) Bertin, D.; Boutevin, B.; Robin, J. J. US Pat. 6,335,401, 2002; Eur. Pat. 906,937, 1999.
(13) Kang, E. T.; Zhang, Y. *Adv. Mater.* **2000**, *12*, 1481.
(14) Matyjaszewski, K.; Xia, J. *Chem. Rev.* **2001**, *101*, 2921.
(15) Hester, J. F.; Banerjee, P.; Won, Y.-Y.; Akthakul, A.; Acar, M. H.; Mayes, A. M. *Macromolecules* **2002**, *35*, 7652.
(16) Chiefari, J.; Chong, Y. K.; Ercole, F.; Krstina, J.; Jeffrey, J.; Le, P. T.; Mayadunne, R. T. A.; Meijs, G. F.; Moad, C. L.; Moad, G.; Rizzardo, E.; Thang, S. H. *Macromolecules* **1998**, *31*, 5559.
(17) Lansalot, M.; Davis, T. P.; Heuts, J. P. *Macromolecules* **2002**, *35*, 7582.
(18) Mayadunne, R. T. A.; Jeffery, J.; Moad, G.; Rizzardo, E. *Macromolecules* **2003**, *36*, 1505.
(19) Wang, A. R.; Zhu, S. P. *J. Polym. Sci., Polym. Chem.* **2003**, *41*, 1553.
(20) Convertine, A. J.; Sumerlin, B. S.; Thomas, D. B.; Lowe, A. B.; McCormick, C. L. *Macromolecules* **2003**, *36*, 4679.
(21) Loiseau, J.; Doerr, N.; Svau, J. M.; Egraz, J. B.; Llauro, M. F.; Ladaviere, C. *Macromolecules* **2003**, *36*, 3066.
(22) Lowe, A. B.; Sumerlin, B. S.; Donovan, M. S.; Thomas, D. B.; Hennauxz, P.; McCormick, C. L. *ACS Symp. Ser.* **2003**, *854*, 586.
(23) Yusa, S.; Shimada, Y.; Mitsukami, Y.; Yamamoto, T.; Morishima, Y. *Macromolecules* **2003**, *36*, 4208.
(24) Li, K. *Chem. Eng. Technol.* **2002**, *25*, 2.
(25) Kim, K. J.; Fane, A. G.; Fell, C. J. D. *Desalination* **1998**, *70*, 229.
(26) Brink, L. E. S.; Elbers, S. J. G.; Robbertsen, T.; Both, P. J. *J. Membr. Sci.* **1993**, *76*, 281.
(27) Ying, L.; Kang, E. T.; Neoh, K. G. *J. Membr. Sci.* **2002**, *208*, 361.
(28) Zhai, G. Q.; Ying, L.; Kang, E. T.; Neoh, K. G. *Macromolecules* **2002**, *35*, 9653.
(29) Ying, L.; Kang, E. T.; Neoh, K. G. *Langmuir* **2002**, *18*, 6416.
(30) Wang, P.; Tan, K. L.; Kang, E. T.; Neoh, K. G. *J. Mater. Chem.* **2001**, *11*, 783.
(31) Strathmann, H.; Kock, K. *Desalination* **1977**, *21*, 241.
(32) Pham, Q.-T.; Petiaud, R.; Llauro, M.-F.; Waton, H. *Proton and Carbon NMR Spectra of Polymers*; John Wiley & Sons: Chichester, UK, 1984; Vol. 3, p 455.
(33) Brondino, C.; Boutevin, B.; Parisi, J. P.; Schrynemackers, J. *J. Appl. Polym. Sci.* **1999**, *72*, 611.
(34) Hester, J. F.; Banerjee, P.; Mayes, A. M. *Macromolecules* **1999**, *32*, 1643.
(35) Sawyer, L. C.; Grubb, D. T. *Polymer Microscopy*; Chapman and Hall: London, 1987.
(36) *Reference Manual of Coulter Porometer II*; Coulter Electronics Limited: Luton, Beds, UK.
(37) Washburn, E. W. *Proc. Natl. Acad. Sci. U.S.A.* **1921**, *7*, 115.
(38) Hester, J. F.; Mayes, A. M. *J. Membr. Sci.* **2002**, *202*, 119.
(39) Wang, P.; Tan, K. L.; Kang, E. T.; Neoh, K. G. *J. Adhes. Sci. Technol.* **2002**, *16*, 111.
(40) Liang, L.; Shi, M. K.; Viswanathan, V. V.; Peurrung, L. M.; Young, J. S. *J. Membr. Sci.* **2000**, *177*, 97.
(41) Arora, N.; Davis, R. H. *J. Membr. Sci.* **1994**, *92*, 247.

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