Synthesis of an Amphiphilic Glucose-Carrying Graft Copolymer and Its Use for Membrane Surface Modification

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ABSTRACT: A graft copolymer of poly(vinylidene fluoride) (PVDF) with a glucose-carrying methacrylate, 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose, was synthesized via the atom transfer radical polymerization technique with commercial PVDF as the macroinitiator. After a treatment with 88% formic acid, the isopropylidenyl groups of the precursor graft copolymer [poly(vinylidene fluoride)-*g*-poly(3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose)] were converted into hydroxyl groups, and this produced an amphiphilic graft copolymer (PVDF-*g*-PMAG) [poly(vinylidene fluoride)-*g*-poly(3-*O*-methacryloyl-α,β-D-glucopyranose)] with glycopolymer side chains and a narrow molecular weight distribution (weight-average molecular weight/number-average molecular weight < 1.29). This glucose-carrying graft copolymer was characterized with Fourier transform infrared, proton nuclear magnetic resonance, gel permeation chromatography, and thermogravimetric analysis. A novel porous membrane prepared from blends of PVDF with PVDF-*g*-PMAG via an immersion–precipitation technique exhibited significantly enhanced hydrophilicity and an anti-protein-adsorption property. The surface chemical composition and morphology of the membrane were studied with X-ray photoelectron spectroscopy and scanning electron microscopy, respectively. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 2914–2923, 2008

Key words: atom transfer radical polymerization (ATRP); biopolymers; blending; branched; fluoropolymers

INTRODUCTION

The graft modification of commercial polymers has attracted much interest in both industry and academia for many years because it offers an effective and versatile strategy for fabricating new materials with improved properties.[1–5] Compared to unmodified commercial polymers, grafting-modified copolymers usually exhibit some improved properties such as compatibility with other polymers, hydrophilicity, wettability, biocompatibility, resistance to the adsorption of protein and other organic molecules, adhesion to the surface of metallic and inorganic substrates, and chemical resistance.[6–8]

Over the past decades, numerous studies have been devoted to the fabrication of graft copolymers with enhanced surface properties. According to the literature, the most common and widely used approach for the preparation of graft copolymers based on commercial polymers is free-radical polymerization.[9–12] Free-radical polymerization is particularly interesting because of its adaptability to a wide range of functional monomers under less stringent synthesis conditions. Unfortunately, the inherent uncontrolled nature of conventional free-radical polymerization inevitably leads to homopolymerization of the comonomers during the reaction process, resulting in a product that is a mixture of homopolymer and graft copolymers. Moreover, some other undesirable side reactions such as gel formation and backbone degradation can occur as a result of uncontrolled free-radical polymerization.[13,14]

In recent years, the rapid development in the field of living/controlled radical polymerization has provided another strategy for fabricating graft copolymers, especially with well-defined structures. In living/controlled radical polymerization, no evidence of homopolymerization has been observed because the concentration of growing radicals is suppressed to avoid termination. As one of the most efficient controlled radical polymerizations, atom transfer radical polymerization (ATRP)[15,16] has recently been explored for fabricating graft copolymers based on polymeric macroinitiators. For instance, Paik et al.[17] successfully grafted styrene and various methyl methacrylates onto a poly[(vinyl chloride)-*co*-(vinyl

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chloroacetate)] commercial polymer through the use of chloroacetate groups as initiation sites for ATRP of the monomers.[17]

It is now clear that carbohydrates are essential constituents in living bodies and play important roles in many recognition events, including blood coagulation, immune response, virus infection, inflammation, fertilization, and embryogenesis, and in nervous systems.[18–20] Synthetic polymers with pendent sugar moieties, which are called glycopolymers, can be used as models for studying the nature of molecular recognition processes between carbohydrates and proteins.[21] Besides this, Zhu and Marchant[22] demonstrated that glycopolymers can be used as antifouling interface materials to reduce platelet adhesion. With this in mind, a variety of glycopolymers have been synthesized by the free-radical polymerization of vinyl monomers with pendent sugar moieties or macromolecular reactions between functional polymers and saccharide derivatives.[23–25] However, it is also known that molecular recognition processes are cooperative and strongly dependent on the spatial distribution of sugar moieties.[26] The random clustering of carbohydrates sometimes significantly affects the strength of affinity with guest proteins, which is ascribed to the steric hindrance of the multiple sugar branches. To elucidate the multivalent interaction between carbohydrates and proteins, it is necessary to control the molecular structure of glycopolymers. Thus, the controlled synthesis of structurally well-defined glycopolymers has been explored by various polymerization techniques such as cationic polymerization[27] and living/controlled free-radical polymerization (ATRP).[23]

Poly(vinylidene fluoride) (PVDF) is one of the most popular synthetic polymers and has many unique properties such as excellent chemical and mechanical stability, thermal stability, fire resistance, and a low dielectric constant.[28] It has been widely used in various fields ranging from micro/ultrafiltration[29–31] to biomedical techniques.[32] However, the application of PVDF materials is strongly limited in some fields such as the treatment of protein-containing solutions and biomedical applications because of its inherent hydrophobicity, which makes PVDF exhibit poor biocompatibility and makes it susceptible to the irreversible adsorption fouling of proteins.[33] To improve the hydrophilicity and biocompatibility of PVDF, different methods have been studied for grafting hydrophilic monomers onto a PVDF backbone. Hester et al.[34] recently successfully fabricated amphiphilic graft copolymers with a PVDF backbone and poly(oxyethylene methacrylate) side chains via the ATRP technique using commercial PVDF as the macroinitiator. The amphiphilic graft copolymers so prepared exhibited excellent hydrophilicity and biocompatibility.

Here we for the first time report the synthesis of a novel glucose-carrying graft copolymer, poly(vinylidene fluoride)-*g*-poly(3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose) (PVDF-*g*-PMAIpG), by ATRP with a commercial PVDF as the macroinitiator. After deprotection treatment, the isopropylidenyl groups of the precursor graft copolymers (PVDF-*g*-PMAIpG) were converted into hydroxyl groups, and this produced an amphiphilic glucose-carrying graft copolymer (PVDF-*g*-PMAG). The synthesis route is outlined in Figure 1. The use of PVDF-*g*-PMAG as a membrane additive for the surface modification of PVDF membranes is also preliminarily explored in this article.

EXPERIMENTAL

Materials

1,2:5,6-Di-*O*-isopropylidene-D-glucofuranose (IpG; 98%) and methacrylic anhydride (98%) were purchased from Alfa Aesar Co. (Beijing, China) and were used without further purification. Poly(vinylidene fluoride) with a number-average molecular weight of 1.07×10^5 g/mol [$PVDF_{107K}$; polydispersity index (PDI) = 2.33], copper(I) chloride (CuCl; 99%), and 4,4′-dimethyl-2,2′-dipyridyl (DMDP; 99%) were purchased from Aldrich and were used as received. Bovine serum albumin (BSA), phosphate-buffered saline, poly(ethylene glycol) with a molecular weight of 600 (PEG600), and pyridine (analytical reagent) were purchased from Shanghai Chemical Regent Co. (Shanghai, China). Pyridine was treated according to the standard procedure[35] before being used; petroleum ether (boiling point range = 30–60°C), 1-methyl-2-pyrrolidinone (NMP; analytical reagent), methanol (analytical reagent), anhydrous ethyl ether (analytical reagent), sodium hydroxide (analytical reagent), anhydrous sodium sulfate (analytical reagent), *N*,*N*-dimethylacetamide (DMAc), and other chemicals were commercially available chemical regents and were used without further purification. All water used in this study was deionized and had a resistivity of 18 MΩ cm. $PVDF_{RF904}$ (number-average molecular weight = 4.7×10^5 g/mol, PDI = 4.39) was offered by 3F New Materials Co. (Shanghai, China).

Synthesis of 3-*O*-methacryloyl-1,2:5,6-di-*O*-isopropylidene-D-glucofuranose (MAIpG)

The synthesis of MAIpG [Fig. 1(a)] was performed with a slight modification of the method reported by Ohno et al.[36] To a stirred solution of IpG (20 g, 76.8 mmol) in 100 mL of dry pyridine, 20 mL (134.2 mmol) of methacrylic anhydride was added dropwise at the ambient temperature. The mixture was

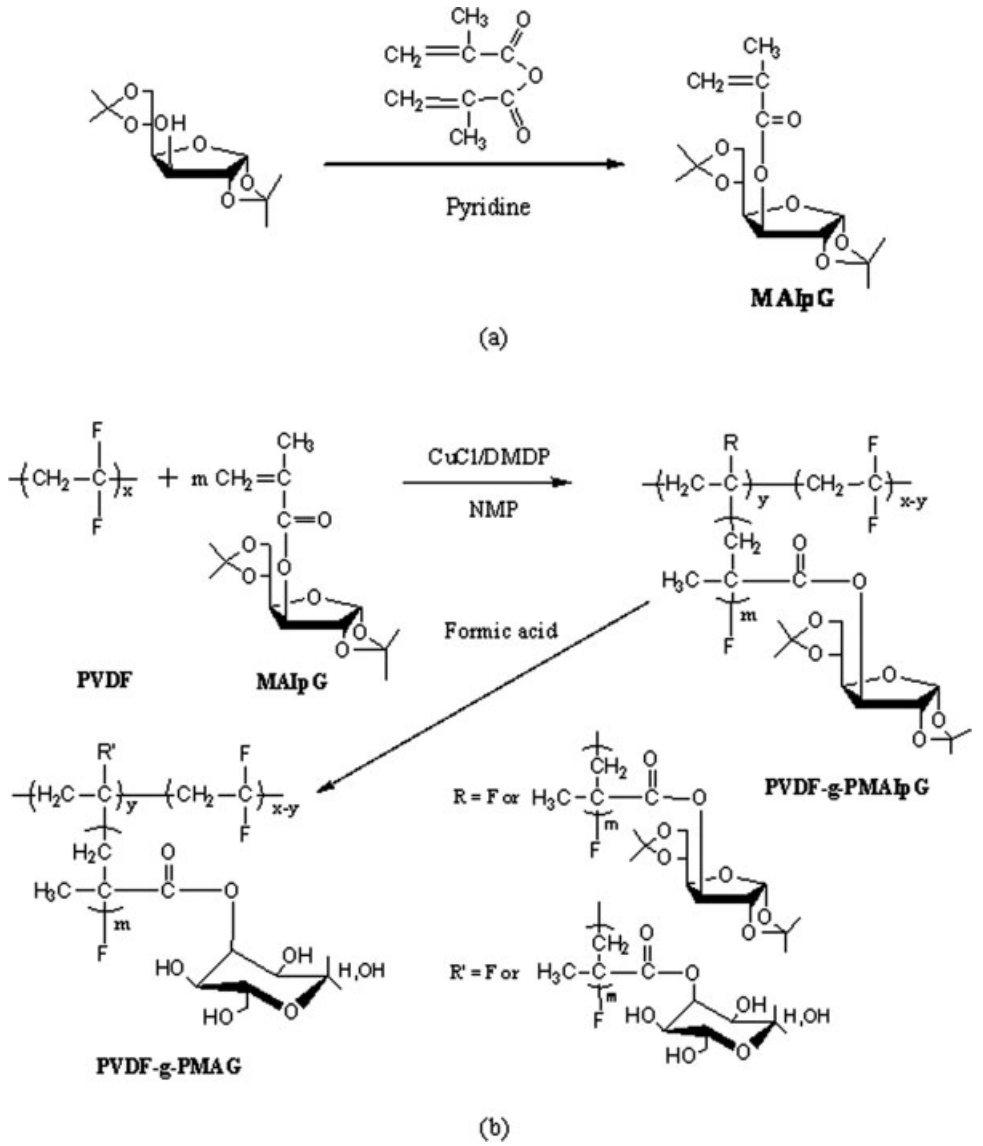

Figure 1 Synthesis of (a) the glucose-carrying methacrylate monomer and (b) the amphiphilic glucose-carrying graft copolymers.

then heated at 65°C for 6 h and for another 2 h after the addition of 70 mL of deionized water. After being stirred overnight at the ambient temperature, the reaction mixture was extracted three times with petroleum ether (boiling point range = 30–60°C, 3 × 100 mL). The combined extracts were washed with a 5% aqueous sodium hydroxide solution (4 × 100 mL) and deionized water (3 × 120 mL) and dried over anhydrous sodium sulfate. After the solvent was evacuated off, the crude product was purified twice by recrystallization from ultrasaturated petroleum ether solutions to yield MAIpG monomers as colorless, transparent crystals, and the MAIpG monomers were further dried *in vacuo* at the ambient temperature for 24 h before being used.

^{1}H-NMR (500 MHz, $CDCl_3$, tetramethylsilane): 1.31 (s, 6H, $2CH_3$), 1.41 (s, 3H, CH_3), 1.53 (s, 3H, CH_3), 1.96 (s, 3H, CH_3), 4.05, 4.08, 4.25, 4.54, 5.30, 5.89 (7H, sugar moiety), 5.63, 6.13 ppm (s, 2H, CH_2=C<). ANAL. Calcd for $C_{16}H_{24}O_7$: C, 58.51%; H, 7.38%. Found: C, 58.64%; H, 7.36%.

Synthesis of the PVDF-*g*-PMAIpG graft copolymer via ATRP [Fig. 1. (b)]

$PVDF_{107K}$ (2.0 g) was dissolved in NMP (20 mL) in a single-necked, round-bottom flask (50 mL) at 65°C. The solution was cooled to the ambient temperature and then transferred to a 100-mL nitrogen-filled Schlenk flask, after which 10 g of the MAIpG monomer, 0.02 g of CuCl, and 0.115 g of DMDP were added; the flask was sealed with a rubber septum, and nitrogen gas was bubbled through the reaction mixture for 45 min during magnetic stirring. Three

TABLE I
Compositions of the Casting Solutions for the Porous Membranes

	Chemical (g)				
Membrane sample	$PVDF_{RF904}$	PVDF-*g*-PMAG	PEG600	DMAc	Coagulant
M0	5	0	0.5	37	30°C H_2O
M1	5	0.25	0.5	36.75	30°C H_2O

freeze–pump–thaw cycles were used to degas the system. The reaction flask was charged with nitrogen at the ambient temperature and then placed in an oil bath preheated to 80°C, and the reaction was allowed to proceed for 24 h. The graft copolymer was precipitated into a mixture of methanol and petroleum ether (1:1 v/v) and then recovered by filtration. The polymer was purified three times by redissolution in NMP and reprecipitation in methanol/petroleum ether. Finally, the polymer was dried *in vacuo* overnight at 35°C.

Preparation of the PVDF-*g*-PMAG amphiphilic graft copolymer

The transformation of PVDF-*g*-PMAIpG graft copolymers into amphiphilic glucose-carrying graft copolymers (PVDF-*g*-PMAG) was carried out as follows. The protected copolymer PVDF-*g*-PMAIpG (3.0 g) was added to 88% formic acid (350 mL) and then stirred for 48 h at the ambient temperature. An additional 150 mL of deionized water was added, and the mixture was stirred for another 3 h; the solvent was partially evacuated off under reduced pressure, and then the concentrated solution was poured into anhydrous ethyl ether (500 mL). The precipitates were recovered by filtration, purified three times by redissolution/reprecipitation in an NMP/anhydrous ethyl ether system, and dried *in vacuo* overnight at the ambient temperature.

Fabrication of the porous membranes

Porous membranes were fabricated via the standard immersion–precipitation technique. First, the casting solutions were prepared by the dissolution of $PVDF_{RF904}$, PVDF-*g*-PMAG, and PEG600 in DMAc and magnetically stirred at 60°C for 8 h. PEG600 acted as a pore-forming agent. The compositions of the casting solutions for different membranes are listed in Table I. After the homogeneous solution was achieved, the casting solutions were left for at least 6 h to allow complete release of gas bubbles. Then, each solution was cast onto a clean glass plate with a stainless steel knife having a 150-μm gate size, and the glass plate was immersed immediately into a coagulation bath of deionized water at 30°C. After coagulation, each membrane was peeled off and washed thoroughly with deionized water to remove the residual solvent and PEG600 and then dried in air at the ambient temperature.

Characterization of the graft copolymers

The Fourier transform infrared (FTIR) spectra were recorded on a Bruker (Ettlingen, Germany) Vector 22 FTIR spectrometer; the PVDF and graft copolymer powders were dispersed in KBr before the measurement. ^{1}H-NMR spectra were recorded on an Avance DMX 500 spectrometer (Bruker) operated at 500 MHz; $CDCl_3$ and DMSO-d_6 were used as solvents, and tetramethylsilane was used as an internal standard. Molecular weights and molecular weight distributions were determined by gel permeation chromatography (GPC), which was conducted at 40°C with water as an eluent (0.80 mL/min), with a Waters 515 pump, Waters Ultrahydrogel columns (500 and 120 in series), and a Waters 2410 refractive-index detector. The calibration was based on a low-polydispersity poly(ethylene oxide) standard. Thermogravimetric analysis (TGA) was performed in a dry nitrogen atmosphere with a PerkinElmer (Germany) Pyris 1 calorimeter, and the TGA thermograms were obtained during heating from 50 to 900°C at 10°C/min.

Characterization of the porous membranes

Scanning electron microscopy (SEM) study

The surface and cross-section morphologies of the neat PVDF membrane and the porous membrane prepared from the blend of the amphiphilic glucose-carrying graft copolymer and PVDF were studied by SEM with a Sirion-100 FEI electron microscope (FEI, Hillsboro, OR). The cross section was fractured in liquid nitrogen. The membrane samples were fixed on the sample plates by double-sided adhesive tape, and a thin layer of gold was sputtered onto the membrane surface and cross section before SEM measurements.

X-ray photoelectron spectroscopy (XPS) analyses

The surface chemical composition of the membranes was analyzed by XPS (PHI5000C; electron spectroscopy for chemical analysis system, Chanhassen, MN)

with Al Kα (hv = 1486.6ev) as the radiation source. The X-ray source was run at a power of 250 W (14.0Kv, 93.9 eV). The measurements were performed at the take-off angle of 45° with respect to the sample plane, survey spectra were collected over the binding energy range of 0–1000 eV, and high-resolution spectra of C1s and O1s were collected. All binding energies were referenced to the CF_2 peak of PVDF at 290.9 eV.

Water contact-angle measurements

The static water contact angles on membranes were measured at room temperature and 65% relative humidity with a contact-angle goniometer (OCA20, Dataphysics Instruments GmbH, Bad Vilbe, Germany); for each contact angle presented, at least 10 sample measurements from different surface locations were averaged.

Protein adsorption measurements

To investigate the anti-protein-adsorption performance of the membrane blended with the glucose-carrying amphiphilic copolymer, the membrane was cut into a round shape with an external area of about 25 cm^2, was washed with a phosphate-buffered saline solution (0.1M phosphate-buffered saline, pH = 7.4) several times, and was then immersed into a 10-mL BSA solution with various concentrations, the pH of which was adjusted to 7.4 with a 0.1M phosphate-buffered saline solution. After incubation at 28°C for 24 h to establish the adsorption equilibrium, the concentration of the BSA solution before and after immersion with the membrane sample was determined with a UV spectrophotometer (UV-1601, Shimadzu, Kyoto, Japan). Then, the apparent adsorbed BSA value for the membrane was calculated.

RESULTS AND DISCUSSION

Synthesis and characterization of the graft copolymers

As schematically illustrated in Figure 1(b), ATRP of the glucose-carrying graft copolymer, PVDF-*g*-PMAIpG, was carried out with PVDF as the macroinitiator, CuCl/DMDP as the catalyst system, and NMP as the solvent. After a treatment with 88% formic acid for 48 h, the isopropylidenyl groups of PVDF-*g*-PMAIpG were converted into hydroxyl groups, and this resulted in the amphiphilic glucose-carrying graft copolymer PVDF-*g*-PMAG.

The FTIR spectra for PVDF, PVDF-*g*-PMAIpG, and PVDF-*g*-PMAG are shown in Figure 2. After the grafting of the glucose-carrying methacrylate monomer onto PVDF, two significant new absorption peaks appeared in the FTIR spectra of PVDF-*g*-PMAIpG; the absorption bands at 2992 and 1735–1740 cm^{-1} are assignable to the C—H stretching of isopropylidenyl groups and C=O stretching of the ester groups, respectively. After deprotection treatment of the precursor polymer PVDF-*g*-PMAIpG, the absorption band of isopropylidenyl groups at 2992 cm^{-1} disappeared, whereas the absorption bands at 1735–1740 cm^{-1}, ascribed to the ester groups, remained unchanged, and a broad absorption peak appeared around 3384 cm^{-1}, which corresponded to the hydroxyl groups formed by the deprotection of the isopropylidenyl groups.

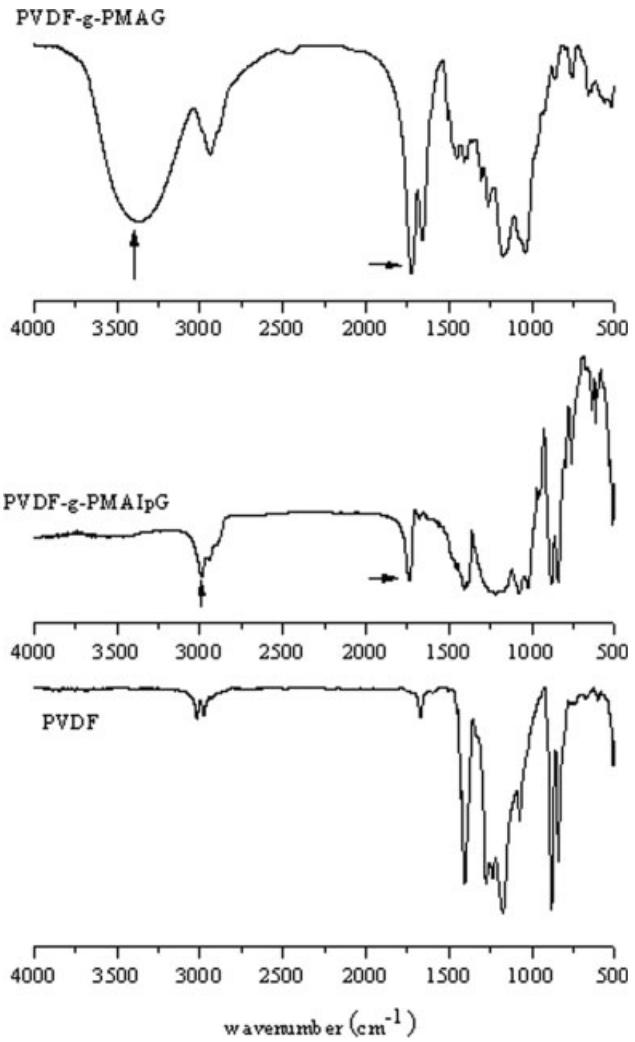

Figure 2 FTIR spectra for PVDF, PVDF-*g*-PMAIpG, and PVDF-*g*-PMAG.

The ^{1}H-NMR spectra for PVDF, PVDF-*g*-PMAIpG, and PVDF-*g*-PMAG are presented in Figure 3. The PVDF spectrum exhibits two well-known peaks related to the head-to-tail and head-to-head bonding arrangements.[37] Grafting of the MAIpG monomer onto PVDF resulted in the appearance of peaks in the regions of 1.3–1.5 and 3.6–6.0 ppm due to the isopropylidene protons and sugar moiety protons of

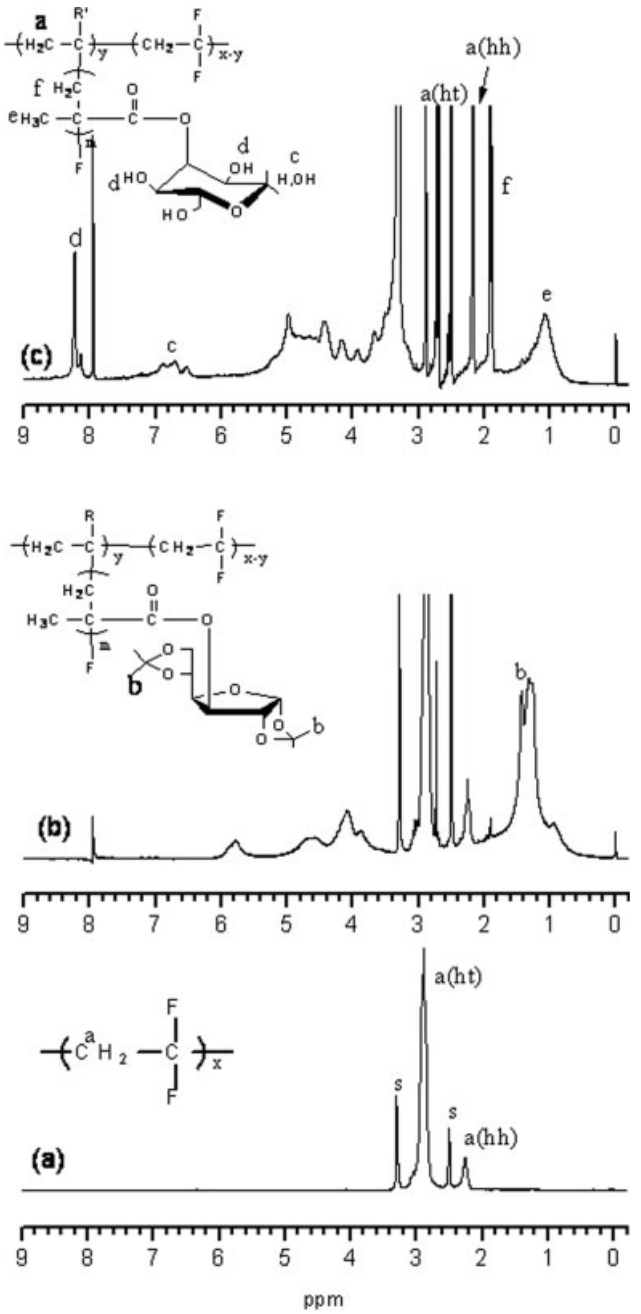

Figure 3 ^{1}H-NMR spectra (500 MHz, DMSO-d_6, and tetramethylsilane) for (a) PVDF, (b) PVDF-*g*-PMAIpG, and (c) PVDF-*g*-PMAG.

the sugar-carrying monomer, respectively. After the acidolysis, the signal ascribed to the isopropylidene protons was entirely absent, and at the same time, the peaks in the region of 6.5–7.0 ppm, which were assignable to the anomeric hydroxyl groups of sugar moieties, appeared. Moreover, the free —OH protons of sugar moieties appeared around 5.0 ppm.[36] The molar fraction of PMAG in the PVDF-*g*-PMAG copolymer was calculated to be 0.496 from Figure 3(c) on the basis of the intensities of resonances *a*(*ht*), *a*(*hh*), and *e*. From the characterization results of FTIR and ^{1}H-NMR presented here, it could be confirmed that MAIpG monomers were grafted onto the PVDF backbone and that the deprotection of isopropylidenyl groups proceeded quantitatively under these experimental conditions.

Because the amphiphilic glucose-carrying graft copolymer synthesized in this study was water-soluble, the determination of the average molecular weights and molecular weight distributions of this copolymer could be performed by GPC with deionized water as the eluent. The GPC results are summarized in Table II. The PDI of the PVDF-*g*-PMAG copolymer (1.29) was fairly low in comparison with the PDI of the PVDF macroinitiator (2.33), suggesting that the ATRP of PVDF-*g*-PMAG under these experimental conditions had a controlled nature. Because of the differences between the hydrodynamic radii of linear polymers and branched polymers of equal molecular weight, the molecular weight deduced from GPC measurements was not an accurate estimate of the true molecular weight of the PVDF-*g*-PMAG copolymer. A more accurate estimate of the number-average molecular weight of the PVDF-*g*-PMAG copolymer ($M_{n,\text{PVDF-}g\text{-PMAG}}$) was obtained from ^{1}H-NMR analysis with the following equation[34]:

$$M_{n,\text{PVDF}-g-\text{PMAG}} = M_{n,\text{PVDF}}\left(1 + x\frac{M_0^{\text{MAG}}}{M_0^{\text{PVDF}}}\right),$$

where $M_{n,\text{PVDF}}$ is the number-average molecular weight of the PVDF macroinitiator obtained from Aldrich; x is the molar ratio of poly(3-*O*-methacryloyl-α,β-D-glucopyranose) (MAG) units to PVDF repeat units in the PVDF-*g*-PMAG copolymer as measured by ^{1}H-NMR; and M_0^{MAG} and M_0^{PVDF} are the repeat unit molar masses of the MAG monomer and PVDF, respectively. $M_{n,\text{PVDF-}g\text{-PMAG}}$ so calculated was $\sim 3.12 \times 10^5$ g/mol.

TGA of the copolymer demonstrated the presence of grafting side chains on the PVDF backbone; the TGA thermograms for the PVDF macroinitiator and

TABLE II
Average Molecular Weights and Molecular Weight Distributions of the PVDF Macroinitiator and Synthesized Glucose-Currying Amphiphilic Graft Copolymer

Polymer	M_n (g/mol)	M_w (g/mol)	M_w/M_n (PDI)
PVDF_{107K}	107,000	250,000	2.33[a]
PVDF-*g*-PMAG	651,121	839,376	1.29[b]

M_n = number-average molecular weight; M_w = weight-average molecular weight.
[a] From the manufacturer.
[b] From GPC and estimated on the basis of low-polydispersity poly(ethylene oxide) standards.

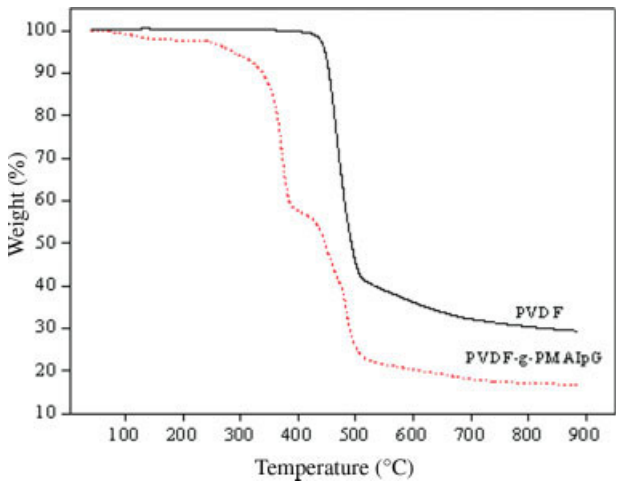

Figure 4 TGA thermograms for the PVDF macroinitiator and PVDF-*g*-PMAIpG. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVDF-*g*-PMAIpG appear in Figure 4, which displays a distinct shoulder corresponding to the higher thermal stability of PVDF in comparison with the grafting side chains of the glucose-carrying methacrylate monomer.

From the combined FTIR, ^{1}H-NMR, GPC, and TGA results discussed here, it can be concluded that the glucose-carrying methacrylate monomer, MAIpG, was actually grafted onto the backbone of the PVDF macroinitiator via ATRP under these experimental conditions.

Preparation and characterization of the porous membranes

Over the past several years, the use of amphiphilic copolymers (including random, alternative, block, graft, and hyperbranched amphiphilic copolymers) as polymer additives for the surface modification of hydrophobic membranes has been a subject of increasing importance in membrane science and technology. Many studies on this subject have demonstrated that during the standard immersion–precipitation process of membrane fabrication, the amphiphilic copolymers are self-segregated to the membrane surface and the surface of internal pore channels.[34,38–41]

Morphology of the porous membranes

The surface and cross-section morphologies of porous membranes fabricated from PVDF and the PVDF/PVDF-*g*-PMAG blend were studied with SEM; SEM micrographs of the separation surfaces and cross sections of membranes cast from the casting solution listed in Table I are shown in Figure 5. The addition of the amphiphilic graft copolymer,

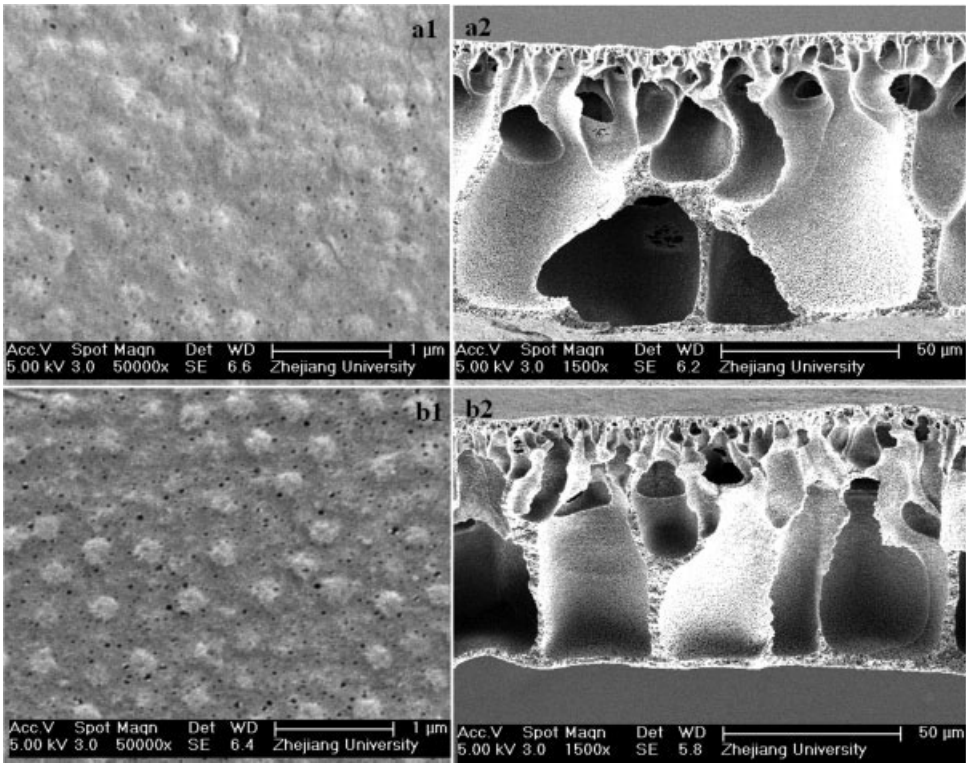

Figure 5 SEM images of the separation surfaces (left) and cross sections (right) of (a) the neat PVDF membrane and (b) the PVDF/PVDF-*g*-PMAG blend membrane (the PVDF-*g*-PMAG content in the blend was ca. 4.76 wt %).

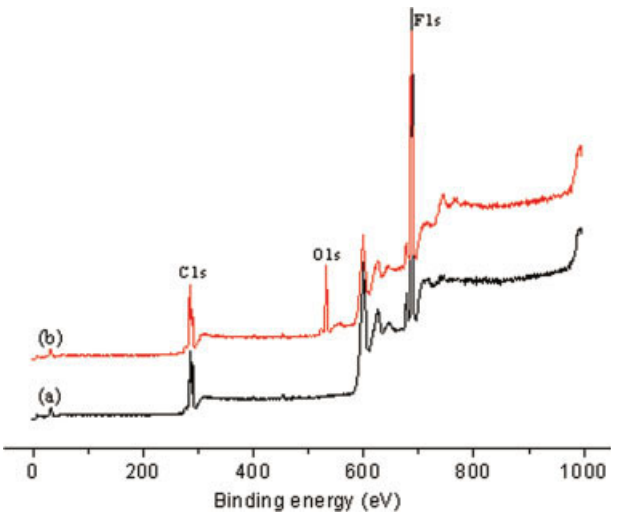

Figure 6 XPS survey scan spectra of (a) the neat PVDF membrane and (b) the PVDF/PVDF-*g*-PMAG blend membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

PVDF-*g*-PMAG, resulted in higher porosity as well as a more uniform pore size distribution on the separation surface of the modified membrane. This enhancement of the membrane porosity and uniform pore size distribution is very advantageous in ultrafiltration processes because it provides higher fluxes and higher rejection ratios.

Surface chemical compositions of the porous membranes

The surface chemical compositions of the porous membranes were analyzed with XPS; the XPS results for the neat PVDF membrane and PVDF/PVDF-*g*-PMAG blend membrane are shown in Figure 6 and Table III. Figure 6 shows the typical XPS spectra of the neat PVDF membrane and PVDF/PVDF-*g*-PMAG blend membrane (the PVDF-*g*-PMAG content in the blend was ca. 4.76 wt %). Both membranes showed peaks corresponding to C1s (binding energy = 285.8 eV) and F1s (binding energy = 688.0 eV), which are typical for PVDF. In comparison with the neat PVDF membrane, the blend membrane showed an extra peak corresponding to O1s (binding energy = 532.0 eV).

TABLE III
XPS Results of the Neat PVDF Membrane and PVDF/PVDF-*g*-PMAG Blend Membrane

Membrane sample	Chemical composition of the membrane surface (XPS)			
	C (wt %)	F (wt %)	O (wt %)	O/F
M0	50.68	49.32	0	0
M1	56.57	31.72	11.71	0.37

The atomic ratio, O/F, provides a measure of the PVDF-*g*-PMAG surface composition. Figure 6 shows that the surface of the neat PVDF membrane had no oxygen signal, indicating that the pore-forming agent PEG600 had leached out from the PVDF membrane during the immersion–precipitation process. In the case of the blend membrane, Table III shows that after blending with a small amount of PVDF-*g*-PMAG (the content of PVDF-*g*-PMAG in the membrane matrix was ca. 4.76 wt %), the oxygen concentration (11.71 mol %) on the surface of the blend membrane increased significantly, and the O/F ratio reached 0.37.

Figure 7 shows the C1s core-level scan spectra of the PVDF/PVDF-*g*-PMAG blend membrane; the C1s core-level spectra are curve-fitted with five components corresponding to C—O, C—COO, COO, CH, CH_2, and CF_2 with binding energies at 286.5, 285.7, 289.3, 285.0, 286.4, and 290.9 eV, respectively. The emergence of C—O, C—COO, and COO peaks in the C1s core-level scan spectra indicates that the water-soluble amphiphilic glucose-carrying copolymer PVDF-*g*-PMAG was maintained on the membrane surface, although this membrane was prepared via an immersion–precipitation process. The near-surface molar fraction of PMAG (0.382) was calculated as follows:

$$\frac{[\mathrm{PMAG}]}{[\mathrm{PMAG}]+[-\mathrm{CH_2}-\mathrm{CF_2}-]}=\frac{A_{\mathrm{COO}}}{A_{\mathrm{COO}}+A_{\mathrm{CF_2}}},$$

where A_{COO} and $A_{\mathrm{CF_2}}$ are the areas of the fitted COO and CF_2 peaks, respectively.

The XPS analyses suggest that the amphiphilic copolymer, PVDF-*g*-PMAG, substantially segregated to

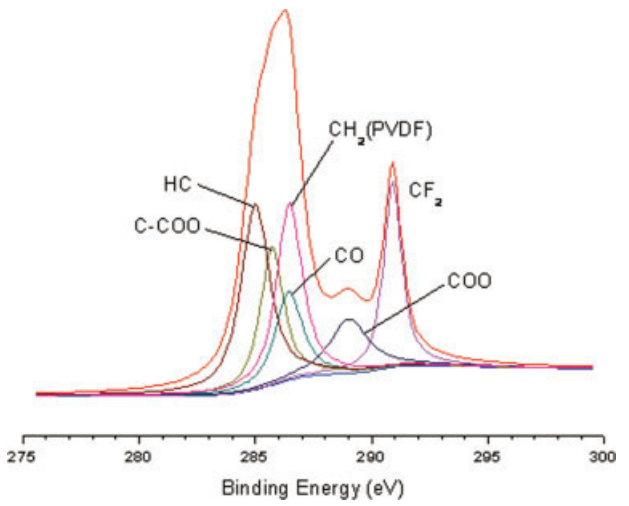

Figure 7 XPS C1s core-level scan spectra of the PVDF/PVDF-*g*-PMAG blend membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

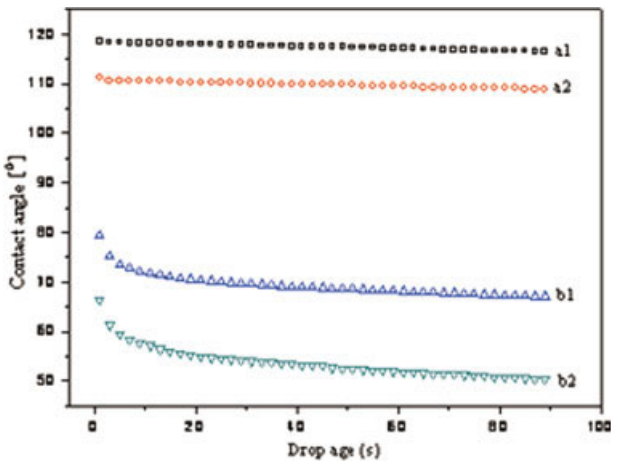

Figure 8 Changes in the water contact angle with the drop age for the neat PVDF membrane and the PVDF/PVDF-*g*-PMAG blend membrane: (a1) bottom surface of the neat PVDF membrane, (a2) separation surface of the neat PVDF membrane, (b1) bottom surface of the PVDF/PVDF-*g*-PMAG blend membrane, and (b2) separation surface of the PVDF/PVDF-*g*-PMAG blend membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the membrane surface during the immersion–precipitation process.

Water contact-angle characterization

Contact-angle measurement is a convenient method for obtaining information about surface characteristics such as the relative hydrophilicity of materials. In general, these measurements are difficult to unpuzzle in the case of porous materials because of contraction in the dry state, capillary forces, heterogeneity and roughness of the surface, and so forth.[42,43] However, the relative hydrophilicity of a polymeric membrane surface can be easily obtained by this method. The changes in hydrophilicity of the PVDF/PVDF-*g*-PMAG blend membrane were examined with the static water contact angle. As can be seen in Figure 8, regardless of the separation surface or bottom surface, the initial static water contact angles decreased significantly after incorporation with the amphiphilic PVDF-*g*-PMAG copolymer. Moreover, Figure 8 shows that the water contact angle of the neat PVDF membrane almost remained unchanged with the change in the drop age, whereas the water contact angles of the blend membrane decreased obviously with the increase in the drop age; this was due to the presence of the amphiphilic PVDF-*g*-PMAG copolymer and more directly due to the hydrophilic nature of the PMAG side chains. Therefore, the hydrophilicity of the blend membrane could be enhanced significantly because of the presence of the amphiphilic graft copolymer.

Static protein adsorption characterization

Figure 9 shows that the amounts of the apparent protein adsorption on the PVDF membrane decreased significantly after incorporation with the amphiphilic PVDF-*g*-PMAG copolymer. The obvious decrease in BSA adsorption is ascribed to the amphiphilic glucose-carrying graft copolymer, which self-segregated to the membrane surface in the immersion–precipitation process, as confirmed by XPS analyses; this made the surface of the blend membrane more hydrophilic than the neat PVDF membrane.

The combined results of water contact angle and BSA adsorption analysis indicate that the membrane prepared from the PVDF/PVDF-*g*-PMAG blend exhibited improved hydrophilicity and anti-protein-adsorption properties in comparison with the pure PVDF membrane. It is interesting that the water-soluble amphiphilic sugar-carrying graft copolymer synthesized in this study was still retained in the membrane matrix even though the blend membranes were fabricated via an immersion–precipitation process. This is different from the results reported previously by other research groups. According to previous reports, when water-soluble polymers are used as membrane additives, they often leach out during the immersion–precipitation process.[44,45] However, in our experiment, the combined XPS, water contact angle, and BSA adsorption results indicated that PVDF-*g*-PMAG was still anchored in the blend membrane. This can be ascribed to the high molecular weights of the PVDF-*g*-PMAG copolymer, which was entangled with the backbone of the PVDF membrane matrix when they were blended together; this hindered the loss of PVDF-*g*-PMAG in the immersion–precipitation process.

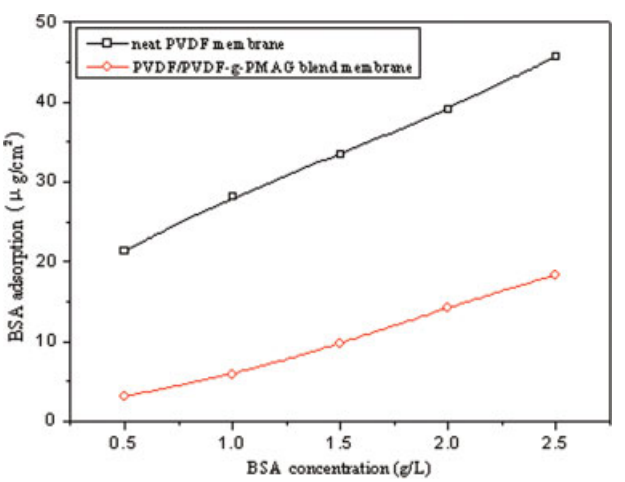

Figure 9 Amount of apparent BSA adsorption on the neat PVDF membrane and the PVDF/PVDF-*g*-PMAG blend membrane. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

CONCLUSIONS

ATRP of a glucose-carrying methacrylate monomer with a commercial PVDF as the macroinitiator for the preparation of a glucose-carrying graft copolymer, PVDF-*g*-PMAIpG, was demonstrated. After acidolysis deprotection treatment of this precursor polymer, a novel amphiphilic glucose-carrying graft copolymer was obtained. The hydrophilic surface modification of a PVDF membrane with PVDF-*g*-PMAG as an additive was explored, and the preliminary results indicated that the membrane fabricated from the blend of PVDF with PVDF-*g*-PMAG exhibited improved hydrophilicity and anti-protein-adsorption property. Work is ongoing to optimize the molecular structure of this novel sugar-carrying graft copolymer with respect to the grafting chain length and grafting density and to develop a more efficient catalyst system. We are also further investigating membrane fabrication parameters such as the concentration of PVDF-*g*-PMAG, coagulation bath composition, coagulation temperature, and annealing conditions with the desire to maximize surface modification while minimizing the use of PVDF-*g*-PMAG additives.

References

1. Uyama, Y.; Kato, K.; Ikada, Y. Adv Polym Sci 1998, 137, 1.
2. Bhattacharyaa, A.; Misra, B. N. Prog Polym Sci 2004, 29, 767.
3. Kunita, M. H.; Rinaldi, A. W.; Girotto, E. M.; Radovanovic, E.; Muniz, E. C.; Rubira, A. F. Eur Polym J 2005, 41, 2176.
4. Dong, Z. X.; Liu, Z. M.; Han, B. X.; He, J.; Jiang, T.; Yang, G. Y. J Mater Chem 2002, 12, 3565.
5. Ceresa, R. J. Block and Graft Copolymerization; Wiley-Interscience: New York, 1973; Vol. I.
6. Kato, K.; Uchida, E.; Kang, E. T.; Uyama, Y.; Ikada, Y. Prog Polym Sci 2003, 28, 209.
7. Yu, W. H.; Kang, E. T.; Neoh, K. G. Langmuir 2005, 21, 450.
8. Xu, G. X.; Lin, S. G. J Macromol Sci Rev Macromol Chem Phys 1994, 34, 555.
9. Knaus, S.; Spoljaric-Lukacic, L.; Liska, R.; Saf, R. Eur Polym J 2005, 41, 2240.
10. Sengupta, S. S.; Parent, J. S.; Mclean, J. K. J Polym Sci Part A: Polym Chem 2005, 43, 4882.
11. Xing, C. M.; Deng, J. P.; Yang, W. T. Macromol Chem Phys 2005, 206, 1106.
12. Galia, A.; Gregorio, R. D.; Spadaro, G.; Scialdone, O.; Filardo, G. Macromolecules 2004, 37, 4580.
13. Wang, P.; Tan, K. L.; Kang, E. T.; Neoh, K. G. J Mater Chem 2001, 11, 783.
14. Wang, X. S.; Luo, N.; Ying, S. K. Polymer 1999, 40, 4515.
15. Matyjaszewski, K.; Xia, J. H. Chem Rev 2001, 101, 2921.
16. Kamigaito, M.; Ando, T.; Sawamoto, M. Chem Rev 2001, 101, 3689.
17. Paik, H. J.; Gaynor, S. G.; Matyjaszewski, K. Macromol Rapid Commun 1998, 19, 47.
18. Disher, B. M.; Won, Y. Y.; Ege, D. S.; Lee, J. M. C.; Bates, F. S.; Disher, D. E.; Hammer, D. A. Science 1999, 284, 14.
19. (a) Imai, Y.; Lasky, L. A.; Rosen, S. D. Nature 1993, 555, 361; (b) Rele, S. M.; Cui, W. X.; Wang, L. C.; Hou, S. J.; Barr-Zarse, G.; Tatton, D.; Gnanou, Y.; Esko, J. D.; Chaikof, E. L. J Am Chem Soc 2005, 127, 10132.
20. Huang, H.; Remsen, E. E.; Kowalewski, T.; Wooley, K. L. J Am Chem Soc 1999, 121, 3805.
21. Okada, M. Prog Polym Sci 2001, 26, 67.
22. Zhu, J. M.; Marchant, R. E. Biomacromolecules 2006, 17, 1036.
23. (a) Vázquez-Dorbatt, V.; Maynard, H. D. Biomacromolecules 2006, 7, 2297; (b) Li, Z. C.; Liang, Y. Z.; Chen, G. Q.; Li, F. M. Macromol Rapid Commun 2000, 21, 375.
24. Qiu, Y.; Zhang, T.; Ruegsegger, M.; Merchang, R. E. Macromolecules 1998, 31, 2016.
25. Kobayashi, A.; Tsuchida, A.; Usui, T.; Akaike, T. Macromolecules 1997, 10, 2016.
26. Kiessling, L. L.; Pohl, N. L. Chem Biol 1996, 3, 71.
27. Yamada, Y.; Yamaoka, K.; Minoda, M.; Miyamoto, T. J Polym Sci Part A: Polym Chem 1997, 35, 751.
28. Dargaville, T. R.; George, G. A.; David, J. T. H.; Whittaker, A. K. Prog Polym Sci 2003, 28, 1355.
29. Buonomenna, M. G.; Macchi, P.; Davoli, M.; Drioli, E. Eur Polym J 2007, 43, 1557.
30. Khayet, M.; Feng, C. Y.; Khulbe, K. C.; Matsura, T. Polymer 2002, 43, 3879.
31. Bottino, A.; Capannelli, G.; Monticelli, O.; Piaggio, P. J Membr Sci 2000, 166, 23.
32. Mao, C.; Zhao, W. B.; Zhu, A. P.; Shen, J.; Lin, S. C. Process Biochem 2004, 39, 1151.
33. Sean, T. K.; Andrew, L.; Zydney, A. L. J Membr Sci 1995, 107, 115.
34. Hester, J. F.; Banerjee, P.; Won, Y. Y.; Akthakul, A.; Acar, M. H.; Mayes, A. M. Macromolecules 2002, 35, 7652.
35. Armarego, W. L. F. Purification of Laboratory Chemicals, 5th ed.; Elsevier: Amsterdam, 2003.
36. Ohno, K.; Tsui, Y.; Fukuda, T. J Polym Sci Part A: Polym Chem 1998, 36, 2473.
37. Pham, Q. T.; Petiaud, R.; Llauro, M. F.; Waton, H. Proton and Carbon NMR Spectra of Polymers; Wiley: Chichester, England, 1984; Vol. 3.
38. Hester, J. F.; Baneerjee, P.; Mayes, A. M. Macromolecules 1999, 32, 1643.
39. Park, J. Y.; Acar, M. H.; Akthakul, A.; Kuhlman, W.; Mayes, A. M. Biomaterials 2006, 27, 856.
40. Hancock, L. F.; Fagan, S. M.; Ziolo, M. S. Biomaterials 2000, 21, 725.
41. Wang, Y. Q.; Wang, T.; Su, Y. L.; Peng, F. B.; Wu, H.; Jiang, Z. Y. Langmuir 2005, 21, 11856.
42. Taniguchi, M.; Pieracci, J. P.; Belfort, G. Langmuir 2001, 17, 4312.
43. Steen, M. L.; Jordan, A. C.; Fisher, E. R. J Membr Sci 2002, 204, 341.
44. Deshmukh, S. P.; Li, K. J Membr Sci 1998, 150, 75.
45. Wang, D.; Li, K.; Teo, W. K. J Membr Sci 1999, 163, 211.