Modification of Polysulfone Membranes via Surface-Initiated Atom Transfer Radical Polymerization and Their Antifouling Properties

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Received 20 February 2008; accepted 2 September 2008
DOI 10.1002/app.29204
Published online 6 November 2008 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Surface-initiated atom transfer radical polymerization (ATRP) was used to tailor the functionality of polysulfone (PSF) membranes. A simple one-step method for the chloromethylation of PSF under mild conditions was used to introduce surface benzyl chloride groups as active ATRP initiators. Covalently tethered hydrophilic polymer brushes of poly(ethylene glycol)monomethacrylate and 2-hydroxyethyl methacrylate and their block copolymer brushes were prepared via surface-initiated ATRP from the chloromethylated PSF surfaces. A kinetic study revealed that the chain growth from the membranes was consistent with a controlled process. X-ray photoelectron spectroscopy was used to characterize the surface-modified membrane after each modification stage. Protein adsorption experiments revealed substantial antifouling properties of the grafted PSF membranes in comparison with the those of the pristine PSF surface. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 1942–1946, 2009

Key words: atom transfer radical polymerization (ATRP); diblock copolymers; proteins; surfaces

INTRODUCTION

Polysulfone (PSF) is one of the most widely used polymers for preparing ultrafiltration membranes. It displays excellent membrane-forming properties, thermal stability, high mechanical strength, and chemical inertness. However, the hydrophobic nature of PSF makes the membranes prone to fouling in protein-contacting applications. One way to prevent bacterial adhesion on PSF biomedical devices is the creation of nonfouling or microbial-repellent surfaces.[1] The ability to manipulate and control the surface properties of PSF is of crucial importance to their widespread application. The incorporation of desirable hydrophilic functionalities onto PSF surfaces can be accomplished via plasma treatment,[2,3] ultraviolet irradiation,[4] the chemical reaction of hydrophilic components onto the PSF surface,[5–8] and hydrophilic polymer coating and blending.[9,10]

The covalent tethering of polymer brushes on solid substrates is an effective method of surface functionalization. Most of the earlier work on the surface modification of polymer substrates by graft copolymerization has been carried out via free-radical-initiated processes.[11] Recent progress in polymer synthesis techniques has made it possible to produce well-defined polymer chains on various substrate surfaces. Cationic polymerization on gold surfaces,[12] anionic polymerization on ceramic surfaces,[13] nitroxide-mediated radical polymerization on silicon surfaces,[14] atom transfer radical polymerization (ATRP) on zirconium surfaces,[15] and reversible addition–fragmentation chain-transfer polymerization on silicate surfaces[16] have been widely used in the synthesis of well-defined living polymers of controlled molecular weights and macromolecular architecture. ATRP has been successfully used to prepare well-defined polymer brushes on various surfaces.[17–21]

In this study, the chloromethylation of PSF chains was first carried out to introduce the ATRP initiators into their backbones and onto the surface. Functional polymer brushes of poly(ethylene glycol)monomethacrylate (PEGMA) and 2-hydroxyethyl methacrylate (HEMA) and their block copolymer brushes were then prepared via surface-initiated ATRP. The modified PSF membranes were characterized by contact angle measurements and X-ray photoelectron spectroscopy (XPS). The antifouling properties of the modified PSF were dramatically improved compared to those of the unmodified membrane.

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EXPERIMENTAL

Materials

PSFs were obtained from Aldrich Chemical Co. (Milwaukee, WI). PEGMA (number-average molecular weight = 360, >99%), HEMA (97%), paraformaldehyde [$(HCOH)_n$; +95%], chlorotrimethylsilane (Me_3SiCl; 97%), stannic chloride $SnCl_4$; 99%), 2,2′-byridine (Bpy; 99%), copper(I) chloride (CuCl; 99%), and copper(II) chloride ($CuCl_2$; 97%) were also obtained from Aldrich Chemical Co. PEGMA and HEMA were passed through an inhibitor-remover column to remove the inhibitors and then stored in clean vessels at −10°C. The solvents were analytical grade and were used without further purification unless otherwise mentioned.

Surface-initiated ATRP polymerization

The chloromethylation of PSF chains was performed to introduce benzyl chloride groups, as shown schematically in Figure 1. For the chloromethylation reaction,[22] 5 g of $(HCOH)_n$, 0.2 mL of $SnCl_4$, and 21 mL of $(CH_3)_3SiCl$ were introduced into the PSF chloroform solution. The mixture was stirred at 50°C for 12 h to produce chloromethylated polysulfone (PSF-Cl) and was then poured into methanol. The precipitate was filtered, redissolved, and reprecipitated and then dried under reduced pressure at 80°C for at least 24 h until a constant weight was obtained.

The membranes were fabricated via the well-known phase-inversion process. The PSF-Cl was solved in NMP to a concentration of 18 wt %. The PSF-Cl solution was cast on a glass plate. The glass plate was subsequently immersed in doubly distilled water. After the membrane had detached from the glass plate, it was extracted in a second water bath. The obtained membrane was kept in distilled water.

For the preparation of surface-initiated ATRP from the PSF-Cl membranes, the reaction was carried out for a predetermined period of time with a 100 : 1 : 0.2 : 1.5 [PEGMA or HEMA]/[CuCl]/[$CuCl_2$]/[Bpy] molar feed ratio in 4 mL of deionized water in a Pyrex tube containing the PSF-Cl membrane at room temperature. After the reaction, the PSF–poly[poly(-ethylene glycol)monomethacrylate] [P(PEGMA)] and PSF–poly(2-hydroxyethyl methacrylate) [P(HEMA)] membranes were washed and extracted well with ethanol and doubly distilled water. Then, the membranes were immersed in a large volume of ethanol for about 48 h to ensure the complete removal of the adhered and physically adsorbed reactants.

To confirm the presence of dormant chain ends in the grafted P(PEGMA) and P(HEMA) brushes, block copolymer brushes were prepared by reactivation of the dormant chain ends on the corresponding PSF–P(PEGMA) and PSF–P(HEMA) membranes to serve as the macroinitiators. The procedure for the second round of surface-initiated ATRP was similar to those used for the surface-initiated ATRP of the initial homopolymer.

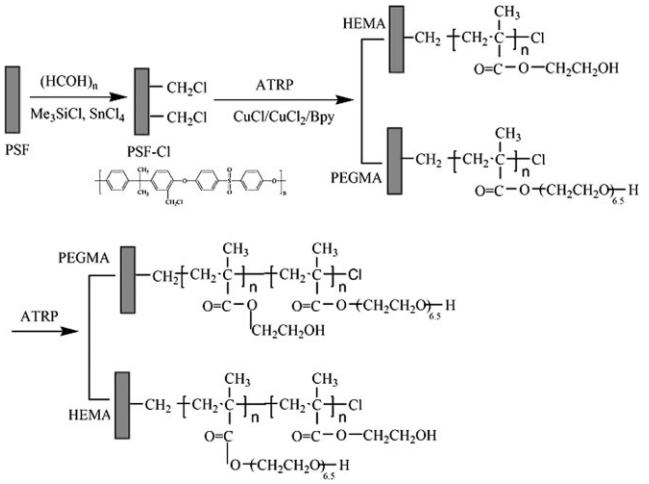

Figure 1 Schematic diagram illustrating the process of surface-initiated ATRP from the PSF membrane.

Protein fouling measurements

To investigate the antifouling properties of the modified PSF membranes, protein fouling experiments were carried out on the membranes with bovine serum albumin (BSA) as a model protein. The membranes were initially washed with phosphate-buffered saline (PBS) solution (0.01*M*, pH 7.4) for 1 h and then incubated in a PBS solution containing 6.0 mg/mL BSA for 24 h at room temperature. The membranes were then removed from the solution, gently washed three times with PBS, and rinsed once with doubly distilled water. After they were dried under reduced pressure, the protein-adsorbed surfaces were analyzed by XPS. The XPS N1s core-level signal was used as a marker for the analysis of the relative amount of protein adsorbed on the surface.[23]

Characterization

XPS analysis was performed on a Kratos AXIS HSi spectrometer (Kratos Analytical Ltd., Manchester, UK) with a monochromotized Al Kα X-ray source (1486.6 eV photons) and procedures similar to those described earlier.[24,25] Surface elemental stoichiometries were determined from the sensitivity-factor-corrected spectral area ratios and were reliable to within ±5%. The static water contact angles of the pristine and functionalized surfaces were measured at 25°C and 60% relative humidity on a telescopic goniometer (Rame-Hart model 10000-230, Rame-Hart, Inc., Mountain Lakes, NJ). The telescope, with a magnification power of 23×, was equipped with a

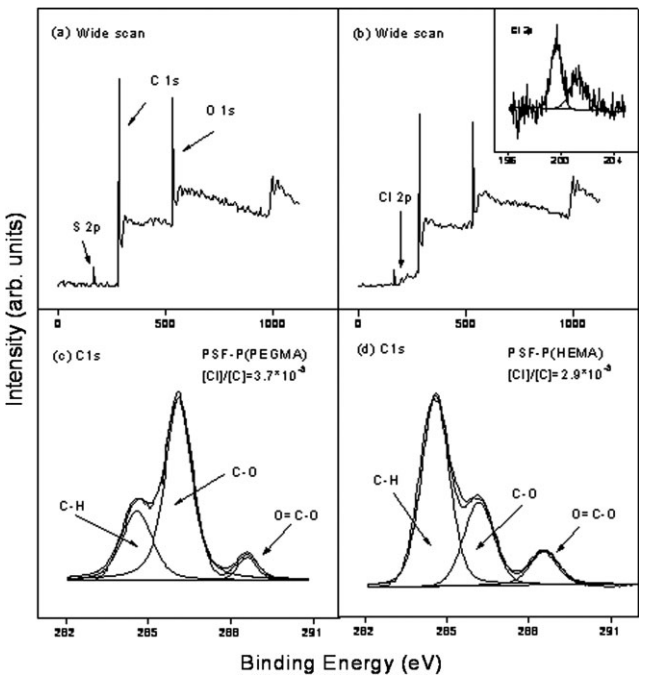

Figure 2 Wide scans of (a) PSF and (b) PSF-Cl membrane surfaces and C1s core-level spectra of (c) PSF–P(PEGMA) and (d) PSF–P(HEMA) surfaces.

protractor of 1° graduation. For each angle reported, at least three measurements from different surface locations were averaged. The angle reported was reliable to ±3°.

RESULTS AND DISCUSSION

Surface-initiated ATRP on PSF membranes

The chemical composition of PSF-Cl was determined by XPS. The XPS wide-scan spectra of the pristine PSF and PSF-Cl surfaces are compared in Figure 2(a,b); the Cl2p signal appeared on the PSF-Cl surface. The corresponding Cl2p core-level spectrum consisted of the Cl2p3/2 and Cl2p1/2 peak components at binding energies of about 199.7 and 201.5 eV, respectively, attributable to the covalently bonded chlorine species.[26] The [Cl]/[C] ratio was about 1.8×10^{-2} (as determined from the sensitivity-factor-corrected Cl2p and C1s core-level spectral area ratio), which confirmed that the active benzyl chloride groups were introduced for the subsequent surface-initiated ATRP. Thus, P(PEGMA) and P(HEMA) were obtained by the surface-initiated ATRP of PEGMA and HEMA on the surface of the PSF-Cl membrane.

The PSF-Cl surfaces after grafting with PEGMA polymer and HEMA polymer were analyzed by XPS, as shown in Figure 2(c,d). The reaction conditions and surface properties of the modified membranes are also summarized in Table I. The C1s core-level spectra of the PSF–P(PEGMA) and PSF–P(HEMA) surfaces were curve-fitted to three peak components with binding energies of about 284.6, 286.2, and 288.6 eV, attributable to the C—H, C—O and O=C—O species, respectively.[26] The [C—O]/[O=C—O] ratios for the PSF–P(PEGMA) and PSF–P(HEMA) surfaces were about 11.5 and 2.1, respectively, which were in approximate agreement with the theoretical ratios of about 12.0 and 2.0 for the corresponding P(PEGMA) and P(HEMA) homopolymers. The XPS results indicate the presence of the grafted P(PEGMA) and P(HEMA) layers on the PSF surfaces with a thickness larger than the probing depth (ca. 7.5 nm in an organic matrix)[27,28] of the XPS technique. *Grafting yield* is defined as $(W_a - W_b)/SA$, where W_a and W_b represent the weights of the dry membrane after and before grafting, respectively, and SA is the respective surface area of the membrane. These values for the PSF–P(HEMA)1 and PSF–P(HEMA)2 membranes were about 5.1 and 14.2 mg/cm^2, respectively. The corresponding grafting yield values for the PSF–P(PEGMA)2 membrane

TABLE I
Static Water Contact Angles, [Cl]/[C] Ratios, and Grafting Yields of Surface-Functionalized PSF

Sample[a]	Reaction time (min)	[Cl]/[C][b]	Grafting yield (mg/cm^2)[c]	Contact angle (±3°)[d]
PSF–P(HEMA)1	30	5.8×10^{-3}	5.1	45
PSF–P(HEMA)2	90	2.9×10^{-3}	14.2	39
PSF–P(PEGMA)1	60	5.0×10^{-3}	7.5	44
PSF–P(PEGMA)2	90	3.7×10^{-3}	10.0	42
PSF–P(HEMA)2–P(PEGMA)[e]	60		14.2 ± 5.8	43
PSF–P(PEGMA)2–P(HEMA)[e]	60		10.0 ± 8.5	40

[a] The reaction conditions were as follows: a monomer/CuCl/CuCl$_2$/Bpy concentration ratio of 100 : 1 : 0.2 : 1.5 in water at room temperature.
[b] Determined from the sensitivity-factor-corrected XPS Cl2p and C1s core-level spectral area ratios. The [Cl]/[C] ratio for the initial PSF-Cl surface was 1.8×10^{-2}.
[c] The grafting yield is defined as $(W_a - W_b)/SA$, where W_a and W_b represent the weights of the dry membrane after and before grafting, respectively, and SA is the respective surface area of the membrane.
[d] The static water contact angle of the pristine PSF was about 79°.
[e] Surface-initiated ATRP from the corresponding PSF–P(HEMA)2 or PSF–P(PEGMA)2 surfaces.

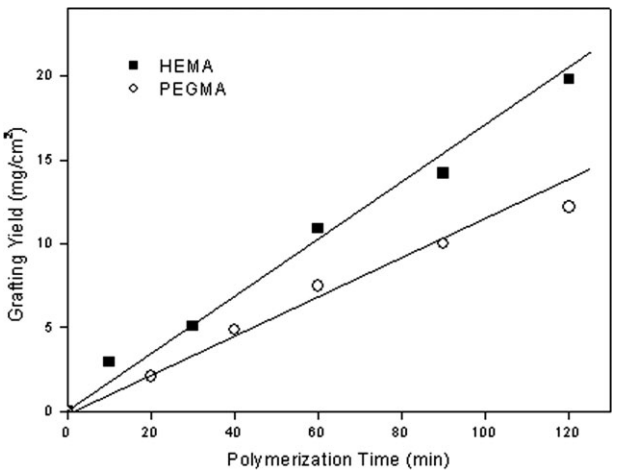

Figure 3 Dependence of the graft yield of the polymer of the grafted PSF membrane on the surface-initiated ATRP time.

surface increased to about 10.0 from about 7.5 mg/cm^2 for the PSF–P(PEGMA)1 membrane surface. After grafting with P(PEGMA) and P(HEMA), the PSF surface became more hydrophilic. The static water contact angles of PSF–P(HEMA)2 and PSF–P(PEGMA)2 were about 39 and 42°, compared to 79° for the pristine PSF surface.

The kinetics of P(PEGMA) and P(HEMA) growth from the PSF-Cl membranes via surface-initiated ATRP were also investigated. Figure 3 shows an approximately linear increase in grafting yield of P(PEGMA) and P(HEMA) on the PSF-Cl membranes with polymerization time, which indicates that the chain growth from the PSF-Cl membrane was in agreement with a living and well-defined process. The growth of the P(HEMA) brushes was faster than that of the P(PEGMA) brushes, which was consistent with the accelerating effect of water on the surface-initiated ATRP of HEMA.[29] With the polymerization time, chain termination by bimolecular coupling or disproportionation reactions resulted in a decrease in the [Cl]/[C] ratio of the grafted PSF surface (Table I).

Block copolymer via consecutive surface-initiated ATRP

The remaining alkyl halides could be reactivated for the preparation of well-defined diblock copolymer brushes in subsequent surface-initiated ATRP to further enhance the functionality of the PSF surface. P(PEGMA)2 and PSF–P(HEMA)2 membranes with a lower density of alkyl halide chain ends were used as the macroinitiators for the second round of surface-initiated ATRP to produce the corresponding PSF–P(PEGMA)2–P(HEMA) and PSF–P(HEMA)2–P(PEGMA) membranes (Fig. 4 and Table I). Both of the C1s core-level spectra of the PSF–P(PEGMA)2–P(HEMA) and PSF–P(HEMA)2–P(PEGMA) membrane surfaces could be curve-fitted into three peak components with binding energies of about 284.6, 286.2, and 288.6 eV, attributable to the C—H, C—O, and O=C—O species, respectively. The C1s core-level spectra of the PSF–P(PEGMA)2–P(HEMA) and PSF–P(HEMA)2–P(PEGMA) membrane surface resembled those of the PSF–P(HEMA)2 and PSF–P(PEGMA)2 membrane surfaces. The grafting yields of the additional P(PEGMA) and P(HEMA) blocks of the corresponding PSF–P(HEMA)2–P(PEGMA) and PSF–P(PEGMA)2–P(HEMA) membranes were about 5.8 and 8.5 mg/cm^2, respectively. Thus, the results indicated that the block copolymer was covalently tethered on the PSF-Cl membrane surface via consecutive surface-initiated ATRP.

Antifouling properties

Polysulfones display nonspecific protein adsorption. Nonspecific protein adsorption is a dominant factor for membrane fouling, and the reduction of protein adsorption enhances the antifouling properties of membranes. In this study, the dense P(HEMA) and P(PEGMA) brushes covalently attached to the PSF membranes shielded the underlying membrane and prevented direct contact of protein molecules with the PSF matrix and reduced protein adsorption. BSA was used as model protein to probe the fouling-resistance ability of the modified and unmodified

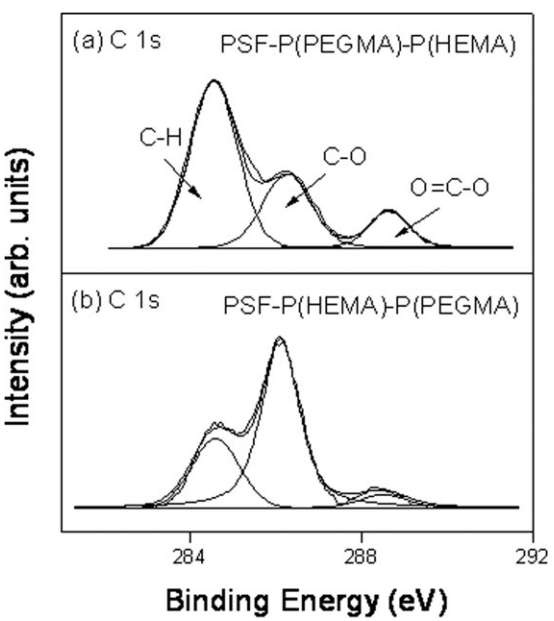

Figure 4 C1s core-level spectra of (a) the PSF–P(PEGMA)2–P(HEMA) surface and (b) the PSF–P(HEMA)2–P(PEGMA) surface.

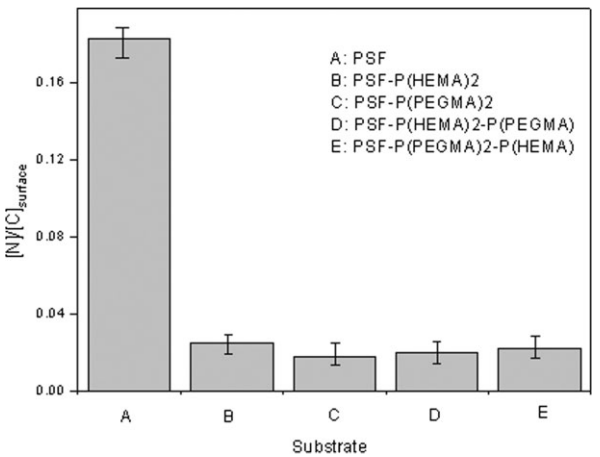

Figure 5 Protein adsorption by (A) pristine PSF and (B) PSF–P(HEMA)2, (C) PSF–P(PEGMA)2, (D) PSF–P(HEMA)2–P(PEGMA), and (E) PSF–P(PEGMA)2–P(HEMA) membranes.

membranes. The relative amount of protein adsorbed onto the surface was represented by the [N]/[C] ratio. The amount of adsorbed BSA decreased remarkably for the various grafted hydrophilic PSF membranes in comparison with the pristine hydrophobic PSF, as shown in Figure 5. The protein was excluded from the hydrophilic layer to prevent the substantial entropy loss caused by the entrance of large protein molecules into the highly structural layer.[30] The presence of hydrophilic P(PEGMA) and P(HEMA) brushes on the PSF surfaces imparted significant resistance to protein adsorption.

CONCLUSIONS

A method for preparing PSF membranes with surface dormant groups for further surface functionalization via ATRP was demonstrated. An approximately linear increase in the graft yield of the functional brushes with polymerization time indicated that the chain growth from the membrane surface was consistent with a controlled process. Protein adsorption experiments revealed that the PSF membranes with grafted hydrophilic P(PEGMA) and P(HEMA) brushes had good antifouling properties.

The authors thank Entang Kang and Koongee Neoh of the National University of Singapore for useful discussions.

References

1. Tedjo, C.; Neoh, K. G.; Kang, E. T.; Fang, N.; Chan, V. J Biomed Mater Res Part A 2007, 82, 479.
2. Wavhal, D. S.; Fisher, E. R. J Membr Sci 2002, 209, 255.
3. Song, Y. Q.; Sheng, J.; Wei, M.; Yuan, X. B. J Appl Polym Sci 2000, 78, 979.
4. Pieracci, J.; Wood, D. W.; Crivello, J. V.; Belfort, G. Chem Mater 2000, 12, 2123.
5. Blanco, J. F.; Sublet, J.; Nguyen, Q. T.; Schaetzel, P. J Membr Sci 2006, 283, 27.
6. Park, J. Y.; Acar, M. H.; Akthakul, A.; Kuhlman, W.; Mayes, A. M. Biomaterials 2006, 27, 856.
7. Hancock, L. F.; Fagan, S. M.; Ziolo, M. S. Biomaterials 2000, 21, 725.
8. Shi, Q.; Su, Y.; Zhu, S.; Li, C.; Zhao, Y.; Jiang, Z. J Membr Sci 2007, 303, 204.
9. Higuchi, A.; Sugiyama, K.; Yoon, B. O.; Sakurai, M.; Hara, M.; Sumita, M.; Sugawara, S.; Shirai, T. Biomaterials 2003, 24, 3235.
10. Kim, Y. W.; Ahn, W. S.; Kim, J. J.; Kim, Y. H. Biomaterials 2005, 26, 2867.
11. Matyjaszewski, K.; Davis, T. P. Handbook of Radical Polymerization; Wiley: Hoboken, NJ, 2002.
12. Jordan, R.; Ulman, A. J Am Chem Soc 1998, 120, 243.
13. Ingall, M. D. K.; Honeyman, C. H.; Mercure, J. V.; Bianconi, P. A.; Kunz, R. R. J Am Chem Soc 1999, 121, 3607.
14. Husseman, M.; Malmstrom, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, J. L.; Mansky, P.; Huang, E.; Russell, T. P.; Hawker, C. J. Macromolecules 1999, 32, 1424.
15. Burkett, S. L.; Ko, N.; Stern, N. D.; Caissie, J. A.; Sengupta, D. Chem Mater 2006, 18, 5137.
16. Baum, M.; Brittain, W. J. Macromolecules 2002, 35, 610.
17. Xu, F. J.; Li, Y. L.; Kang, E. T.; Neoh, K. G. Biomacromolecules 2005, 6, 1759.
18. Edmondson, S.; Osborne, V. L.; Huck, W. T. S. Chem Soc Rev 2004, 35, 14.
19. Ejaz, M.; Ohno, K.; Tsujii, Y.; Fukuda, T. Macromolecules 2000, 33, 2870.
20. Zhao, B.; He, T. Macromolecules 2003, 36, 8599.
21. Wang, J. Y.; Chen, W.; Liu, A. H.; Lu, G.; Zhang, G.; Zhang, J. H.; Yang, B. J Am Chem Soc 2002, 124, 13358.
22. Avram, E. Polym-Plast Technol Eng 2001, 40, 275.
23. Zhai, G.; Kang, E. T.; Neoh, K. G. Macromolecules 2004, 37, 7240.
24. Xu, F. J.; Kang, E. T.; Neoh, K. G. Macromolecules 2005, 38, 1573.
25. Xu, F. J.; Yuan, Z. L.; Kang, E. T.; Neoh, K. G. Langmuir 2004, 20, 8200.
26. Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. Handbook of X-Ray Photoelectron Spectroscopy; PerkinElmer: Eden Prairie, MN, 1992.
27. Tan, K. L.; Woon, L. L.; Wong, H. K.; Kang, E. T.; Neoh, K. G. Macromolecules 1993, 26, 2832.
28. Clark, D. T.; Dilks, A. J Polym Sci Polym Chem Ed 1979, 17, 957.
29. Huang, W. X.; Kim, J. B.; Bruening, M. L.; Baker, G. L. Macromolecules 2002, 35, 1175.
30. Yoshikawa, C.; Goto, A.; Tsujii, Y.; Fukuda, T.; Kimura, T.; Yamamoto, K.; Kishida, A. Macromolecules 2006, 39, 2284.