Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Surface-initiated Atom-transfer Radical Polymerization from Polyimide Films and Their Anti-fouling Properties

Liang Li[a]; Guoping Yan[a]; Jiangyu Wu[a]; Xianghua Yu[a]; Qingzhong Guo[a]
[a] School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan, P.R. China

To cite this Article Li, Liang , Yan, Guoping , Wu, Jiangyu , Yu, Xianghua and Guo, Qingzhong(2008) 'Surface-initiated Atom-transfer Radical Polymerization from Polyimide Films and Their Anti-fouling Properties', Journal of Macromolecular Science, Part A, 45: 10, 828 — 832

To link to this Article: DOI: 10.1080/10601320802300610

URL: http://dx.doi.org/10.1080/10601320802300610

Journal of Macromolecular Science®, Part A: Pure and Applied Chemistry (2008) **45**, 828–832

ISSN: 1060-1325 print / 1520-5738 online
DOI: 10.1080/10601320802300610

Taylor & Francis
Taylor & Francis Group

Surface-initiated Atom-transfer Radical Polymerization from Polyimide Films and Their Anti-fouling Properties

LIANG LI, GUOPING YAN, JIANGYU WU, XIANGHUA YU and QINGZHONG GUO

School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, P.R. China

Received March 2008, and accepted April 2008

A simple one-step method for the chloromethylation of polyimide (PI) under mild conditions was used to introduce benzyl chloride groups into PI film surface. Covalently tethered hydrophilic polymer brushes of poly(ethylene glycol) monomethacrylate (PEGMA) and glycidyl methacrylate (GMA) were prepared via surface initiated atom-transfer radical polymerization (ATRP) from the chloromethylated PI surfaces using benzyl chloride groups as the active ATRP initiators. A kinetics study indicated that the chain growth from the films was in agreement with a controlled process. The dormant chain ends of the grafted polymer on the PI films could reinitiate the consecutive surface-initiated ATRP to prepare surface-functionalized diblock copolymer brushes on the PI films. The modified surface was characterized by X-ray photoelectron spectroscopy (XPS) after each modification stage. Protein adsorption experiments indicated that the PI-P(PEGMA) membrane exhibited substantially improved anti-fouling properties compared to the pristine PI surface.

Keywords: Surface-initiated ATRP, polyimide, diblock copolymer, protein antifouling

1. Introduction

Polyimide (PI) is one of the most widely used polymers because of its good thermal, mechanical, physicochemical, and dielectric properties. It has attracted considerable attention in the applications of membranes, electronics and optics and in the aerospace industry (1–5). The ability to manipulate and enhance the properties of PI is of great importance to its widespread applications. Surface modification is a method applicable to implant technology because it can enhance the functionality of a material surface through proper molecular design, while keeping the bulk properties intact. Many methods have been used to incorporate desirable functionalities onto PI surfaces, such as plasma treatment (6, 7), UV irradiation (8), ion implatation (9, 10) etc. Covalent tethering of polymer brushes on solid substrates is an effective method of surface functionalization. With the progress in polymerization methods (11), cationic polymerization (12), anionic polymerization (13), nitroxide-mediated radical polymerization (14), atom transfer radical polymerization (ATRP) (15), and reversible addition-fragmentation chain-transfer (RAFT) polymerization (16) have been widely used in the synthesis of well-defined "living" polymers with controlled molecular weights and macromolecular architecture on various substrate surfaces. Surface initiated ATRP has been successfully used to prepare well-defined polymer brushes on various surfaces (17–19). A prerequisite for this method is the introduction of ATRP initiators on the substrate chain or surface. Electrophilic substitutions of the aromatic rings in the main chain of PIs, by chloromethylation, can obtain benzyl chloride initiators on PI chains (20, 21).

In the present study, chloromethylation of PI chains was first carried out to introduce the ATRP initiators onto the surface. Functional polymer brushes of poly(ethylene glycol) monomethacrylate (PEGMA) and glycidyl methacrylate (GMA) were then prepared via surface-initiated ATRP. The dormant chain ends of the grafted polymer on the PI films could be reactivated for the consecutive surface-initiated ATRP to prepare surface-functionalized diblock copolymer brushes. Static contact angle measurements and X-ray photoelectron spectroscopy (XPS) were used to characterize the modified PI films. Through bovine serum albumin (BSA) solution adsorption experiments, the PI-P(PEGMA) films showed great protein resistance in comparison with the pristine PI surface.

2. Experimental

2.1. *Materials*

Polyimide films were obtained from DuPont Chemical Co. as Kapton. The structure of a repeat unit of the PI film is

---

Address correspondence to Liang Li, School of Materials Science and Engineering, Wuhan Institute of Technology, Wuhan 430073, P.R. China. E-mail: msell08@163.com

$C_{22}H_{10}N_2O_5$. The PI films were cut into rectangular strips (about 1.5 cm × 2 cm). To remove the organic residues on the surface, the PI films were washed with acetone, methanol, and doubly distilled water in that order. The films were dried under reduced pressure at room temperature for about 24 h and then stored in a dry box. Poly(ethylene glycol) monomethacrylate macromonomer (PEGMA, $M_n = 360$), glycidyl methacrylate (GMA), 2,2,2-trifluoroethyl methacrylate (TFEMA), paraformaldehyde ((HCOH)n), chlorotrimethylsilane (Me_3SiCl), stannic chloride ($SnCl_4$), 2,2′-byridine (Bpy), copper(I) chloride (CuCl), and copper(II) chloride ($CuCl_2$) were purchased from Aldrich Chemical Co. Monomers were passed through an inhibitor-remover column and then stored in clean vessels at −10°C. The solvents were of analytical grade and were used without further purification unless otherwise mentioned.

2.2. *Surface-initiated ATRP polymerization*

The reactions involved were illustrated schematically in Figure 1. The chloromethylation of PI chains was conducted according to the reported procedures (22, 23) to produce the chloromethylated PI surface (PI-Cl). The introduced benzyl chloride groups can serve as initiators for the surface initiated atom transfer radical polymerization (ATRP).

For the preparation of surface-initiated ATRP of PEGMA and GMA from the PI-Cl films, the reaction was carried out for a predetermined period of time using a 100:1:0.2:1.5 [PEGMA or GMA]/[CuCl]/[$CuCl_2$]/[Bpy] molar feed ratio in 5 mL of deionized water (or DMF/water (1:1, v/v)) at room temperature. After the reaction, the PI-P(PEGMA) and PI-P(GMA) films were removed from the reaction mixture and extracted thoroughly with excess ethanol and doubly distilled water (for PI-P(PEGMA)) and acetone (for PI-P(GMA)) over 10 h to ensure the complete removal of the physically adsorbed reactants.

To confirm the presence of dormant chain ends in the grafted polymer brushes, P(PEGMA)-P(TFEMA) block copolymer brushes were prepared by reactivating the dormant chain ends on the corresponding PI-P(PEGMA) films as the macro initiators. The second round of surface initiated ATRP was carried out at 70°C for 10 h in DMF solution containing PI-P(PEGMA) film.

2.3. *Protein fouling measurements*

The PI-P(PEGMA) films were exposed to solutions containing bovine serum albumin (BSA) to investigate the antifouling properties. The membranes were initially washed with phosphate-buffered saline solution (PBS, 0.01 M, pH: 7.4) for 1 h and then immersed in PBS solution containing 8.0 mg/mL BSA for 24 h at room temperature. After the protein adsorption, the membrane was removed and dried under reduced pressure for 48 h. The amount of protein absorbed on the membrane was evaluated by the weight gain after protein adsorption (24).

2.4. *Characterization*

The pristine and modified PI surfaces were characterized by X-ray photoelectron spectroscopy (XPS). XPS was performed on a Kratos AXIS HSi spectrometer with a monochromotized Al Kα X-ray source (1486.6 eV

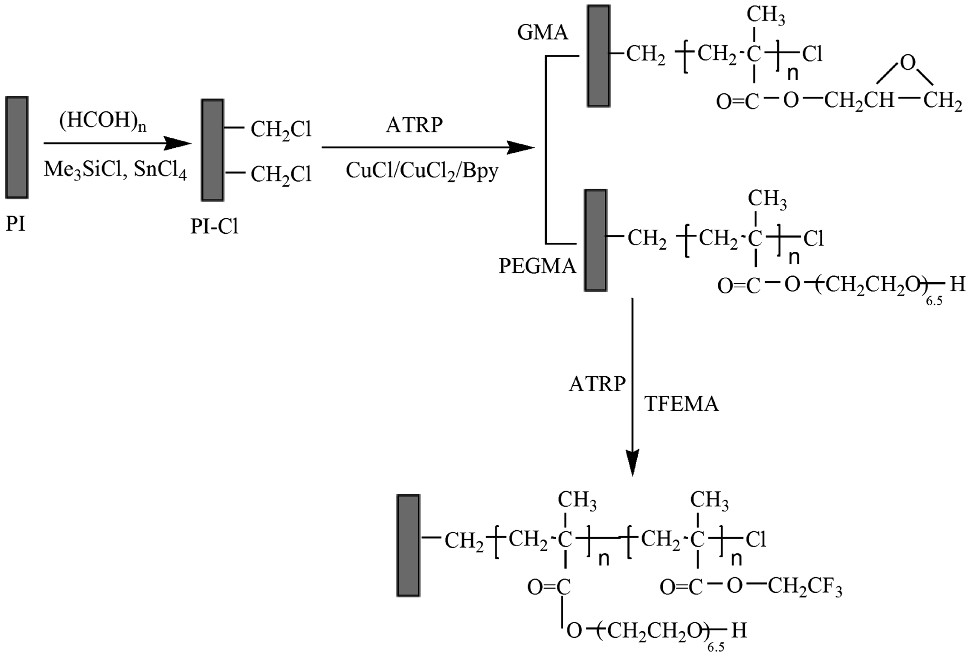

Fig. 1. Schematic diagram illustrating the process of surface-initiated ATRP from the PI film.

photons) and procedures similar to those described earlier (25). The pressure in the analysis chamber was kept at 10-8 Torr or lower during each measurement. Surface elemental stoichiometries were determined from the sensitivity factors-corrected spectral area ratios and were reliable to within ±5%. The static water contact angles were measured at 25°C and 60% relative humidity on a telescopic goniometer (Rame-Hart model 10000-230). The telescope with a magnification power of 23× was equipped with a protractor of 1° graduation. At least four measurements from different surface positions were averaged for each angle reported. The angle reported was reliable to ±3°.

3. Results and discussion

3.1. *Surface-initiated ATRP on PI films*

Benzyl chloride is an effective initiator for surface-initiated ATRP from a variety of substrates. PI films were first chloromethylated in a simple one-step process to introduce the benzyl chloride groups as the active ATRP initiators to produce the well-defined polymer brushes. The chemical composition of the chloromethylated PI was studied by XPS. Figure 2(a and b) showed the Cl 2p core-level spectra of the pristine PI and PI-Cl surfaces. The Cl 2p signal appeared on the PI-Cl surface. The corresponding Cl 2p core-level spectrum consisted of the Cl 2p3/2 and Cl 2p1/2 peak components at the BE of about 199.7 and 201.5 eV, respectively, attributable to the covalently bonded chlorine species (26). The C 1s core-level spectra of the PI surfaces can be curve-fitted into several peak components with BE of about 284.6, 285.6, 286.2, and 288.6 eV, attributable to the C-H, C-N, C-O and N(C=O)$_2$ species, respectively (26). The $\pi - \pi^*$ shakeup satellite was also discernible at BE of about 291 eV, which was associated with the aromatic ring of PI chains. The [Cl]/[C] ratio was about 1.7×10^{-2}, which was determined from the sensitivity-factor-corrected Cl 2p and C 1s core-level spectral area ratio. It indicated that the active benzyl chloride groups were introduced onto the PI film surface. Thus, the polymer could be prepared by surface-initiated atom transfer radical polymerizations (ATRP) of the corresponding monomer from the surface of the PI-Cl films.

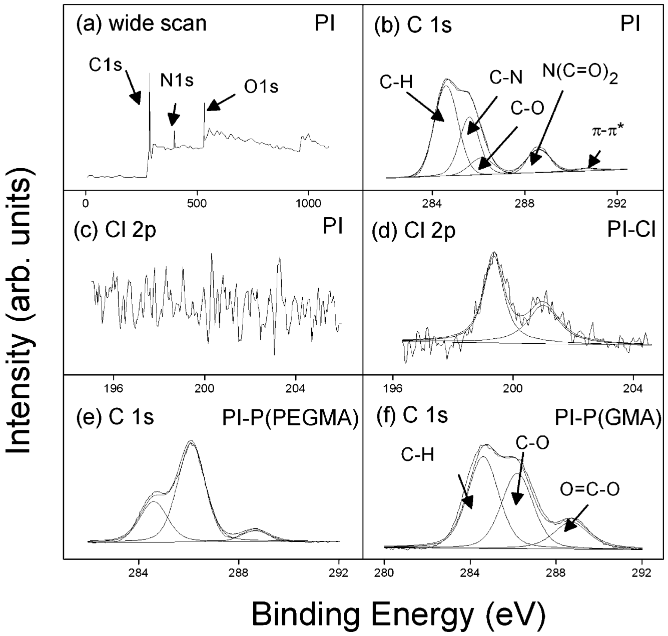

Fig. 2. Wide scan (a), C 1s (b) and Cl 2p (c) core-level spectra of PI, Cl 2p core-level spectra of (d) PI-Cl surfaces, C 1s core-level spectra of (e) PI-P(PEGMA) and (f) PI-P(GMA) surfaces.

The physicochemical properties of the PI films can be tailored by various functional polymers. PEGMA polymer (P(PEGMA)) is recognized as a biomaterial due to its non-interacting nature with proteins and cells (17) and GMA polymer (P(GMA)) is a known surface linker and spacer for biomolecules (27, 28). For surface-initiated ATRP, the initiator concentration on a surface is usually lower than that used in bulk or solution ATRP. An excess amount of deactivating Cu(II) complex is added to quickly establish an equilibrium between the dormant and active chains during surface-initiated ATRP (17). In this work, the ratio of [PEGMA or GMA (monomer)]/[CuCl (catalyst)]/[CuCl$_2$ (deactivator)]/[Bpy (ligand)] was controlled at 100:1:0.2:1.5. The PI-Cl surfaces after grafted with P(PEGMA) and P(GMA) were analyzed by XPS and static contact angle measurements. The reaction conditions and surface properties of the modified membranes were summarized in Table 1. Figure 2c and 2d showed the C 1s core-level spectra of the PI-P(PEGMA) and PI-P(GMA) surfaces. The C 1s core-level spectra of the PI-P(PEGMA) and PI-P(GMA) surfaces can be curve-fitted with three peak components having BEs at about 284.6, 286.2, and 288.6 eV, which were attributable to the C-H, C-O, and O=C-O species, respectively (26). The [O=C-O]/[C-O] ratio for the PI-P(PEGMA) and PI-P(GMA) surfaces were approximate consistent with the theoretical ratios for the corresponding P(PEGMA) and P(GMA) homopolymers. The XPS results suggested that the grafted P(PEGMA) and P(GMA) layers was present on the PI surfaces with a thickness larger than the probing depth (about 7.5 nm in an organic matrix) (25, 29–31) of the XPS technique. Grafting yield was defined as (W_a-W_b)/SA, where W_a and W_b were the weights of the dry film after and before grafting, respectively, and SA was the respective surface area of the film. These values for the PI-P(GMA)1 and PI-P(GMA)2 films are about 7.1 mg/cm^2 and 17.2 mg/cm^2, respectively. The corresponding grafting yield values for the PI-P(PEGMA)2 film increased to about 9.7 mg/cm^2 from about 7.3 mg/cm^2 for the PI-P(PEGMA)1 film. After grafted with P(PEGMA) and P(GMA), the contact angle of PI surface also changed. The static water contact angles of the PI-P(GMA) and PI-P(PEGMA) were about 69° and 42°, compared to 65° for the pristine PI surface.

Table 1. Static water contact angle, [Cl]/[C] ratio and grafting yield of the surface-functionalized PI

Sample[a]	*Reaction Ttime (min)*	*[Cl]/[C]*[b]	*Grafting Yield* (mg/cm^2)[c]	*Contact Angle* (±3°)[d]
PI-P(GMA)1	30	5.4×10^{-3}	7.1	66
PI-P(GMA)2	80	2.1×10^{-3}	17.2	69
PI-P(PEGMA)1	60	4.5×10^{-3}	7.3	44
PI-P(PEGMA)2	90	3.1×10^{-3}	9.7	42
PI-P(PEGMA)2-P(TFEMA)[e]				86

[a] Reaction conditions: 100:1:0.2:1.5 [monomer]/[CuCl]/[$CuCl_2$]/[Bpy] in water at room temperature. [b] Determined from the sensitivity factor-corrected XPS Cl 2p and C 1s core-level spectral area ratios. The [Cl]/[C] ratio for the initial PI-Cl surface is 1.7×10^{-2}. [c] 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 PI is about 65^{circ}. [e] Surface-initiated ATRP from the corresponding PI-P(PEGMA)2 surfaces.

The kinetics of P(PEGMA) and P(GMA) growth from the PI-Cl films via surface-initiated ATRP was also studied. Figure 3 showed the dependence of grafting yield of the P(PEGMA) and P(GMA) on the PI-Cl films on polymerization time. An approximately linear increase with polymerization time suggested that the chain growth of P(PEGMA) and P(GMA) from the PI-Cl membrane was in agreement with a well-defined process.

One of the unique advantages of ATRP is the preservation of the dormant end groups throughout the polymerization reaction. The remaining alkyl halide groups can reinitiate the subsequent surface-initiated ATRP for the preparation of well-defined diblock copolymer brushes to further enhance the functionality of the PI surface. As shown in Figure 4 and Table 1, the PI-P(PEGMA)2 films 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 PI-P(PEGMA)2-P(TFEMA) films. The C 1s core-level spectra of the PI-P(PEGMA)2-P(TFEMA) surfaces can be curve fitted into four peak components with BE at about 284.6, 286.7, 288.7, and 292.5 eV, attributable to the C-H, CF_3-C-O, O=C-O, and C-F_3 species, respectively (26). the [CF_3-C-O]:[O=C-O]:[C-F_3] ratio of the PI-P(PEGMA)2-P(TFEMA) surface was in agreement with the theoretical ratio of the P(TFEMA) homopolymer. Moreover, it turned hydrophobic for the PI-P(PEGMA)2-P(TFEMA) surface (contact angle about 86°) from the hydrophilic PI-P(PEGMA)2 surface (contact angle about 42°). Thus, the results indicated that the block copolymer had been covalently tethered on the PI-Cl film surface via consecutive surface-initiated ATRP from the dormant sites at the grafted P (PEGMA) chain ends.

3.2. *Protein resistance*

BSA was used as a model protein to evaluate the properties of protein resistance of modified and unmodified PI films. The amount of adsorbed BSA was remarkably decreased for the grafted hydrophilic PI-P(PEGMA) films in comparison with the pristine hydrophobic PI, as shown in Figure 5. The amount of the adsorbed BSA was about an

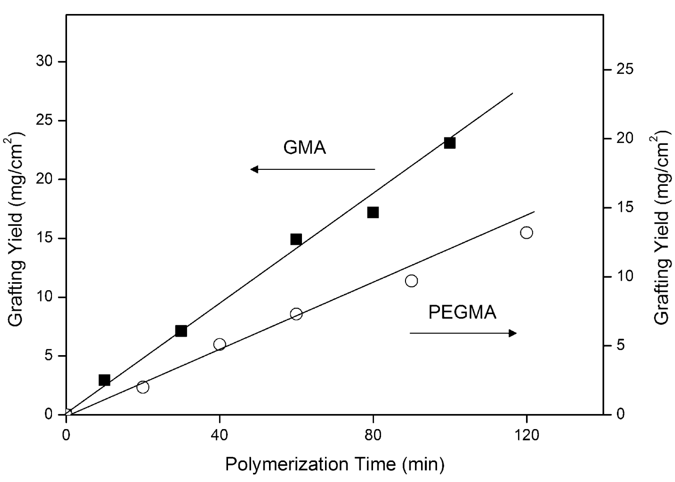

Fig. 3. Dependence of the graft yield of the polymer of the grafted PI on the surface-initiated ATRP time.

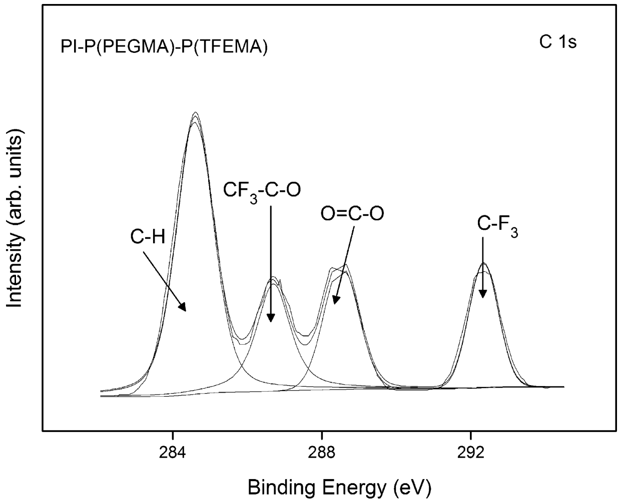

Fig. 4. C 1s core-level spectra of the PI-P(PEGMA)-P(TFEMA) surface.

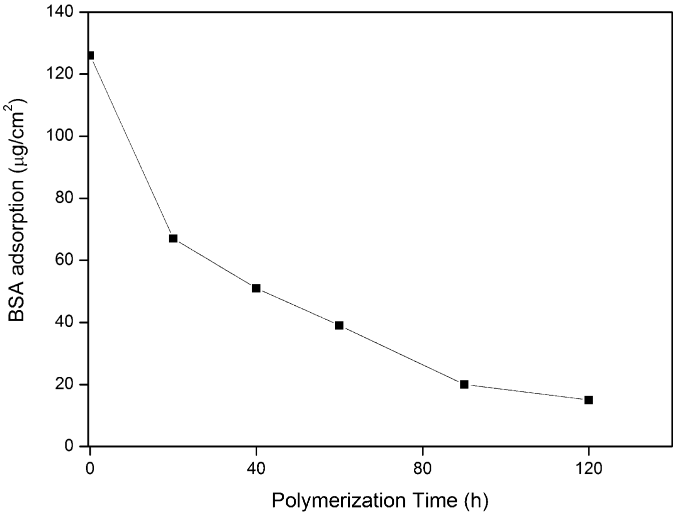

Fig. 5. Protein adsorption by the PI-P(PEGMA) films.

approximately 6-fold reduction after more than 90 min of ATRP of PEGMA. The large excluded volume of the PEG molecules and comb-like, rapidly moving PEG chains in water tend to repel protein molecules approaching the substrate surface (32). The P(PEGMA) brushes covalently attached to the PI membranes prevented direct contact of protein molecules with the PI matrix and imparted significant resistance to protein adsorptions on the PI surfaces.

4. Conclusions

PI films were chloromethylated to get benzyl chloride groups as initiators for atom transfer radical polymerization (ATRP). Functional polymers, as well as their block copolymer brushes, were prepared by surface initiated ATRP from the chloromethylated PI film surfaces. Protein adsorption experiments revealed that the PI films with grafted hydrophilic P(PEGMA) brushes had good protein resistance properties. The chloromethylated PI films with the active ATRP initiators opens up opportunities for the functionalization of films via surface molecular design.

References

1. Maier, G. (2001) *Prog. Polym. Sci.,* 26, 3–65.
2. Ohya, H., Kudryyavtsev, V.V. and Semenova, S.I. Polyimide Membranes: Applications, Fabrications and Properties, Kodansha Ltd: Tokyo, 1996.
3. Luo, J.D., Haller, M., Li, H.X., Tang, H.Z., Jen, A.K.Y., Jakka, K., Chou, C.H. and Shu, C.F. (2004) *Macromolecules*, 37, 248–250.
4. Khalil, M., Saeed, S. and Ahmad, Z. (2007) *J. Macromol. Sci. A*, 44, 55–63.
5. Deligoz, H., Yalcinyuva, T., Ozgumus, S. and Yildirim, S. (2006) *Eur. Polym. J.*, 42, 1370–1377.
6. Lin, Y.S., Liu, H.M. and Chen, H.T. (2006) *J. Appl. Polym. Sci.*, 99, 744–755.
7. Inagaki, N., Tasaka, S. and Baba, T. (2001) *J. Adhes. Sci. Technol.*, 15, 749–762.
8. Lu, Q.H., Li, M., Yin, J., Zhu, Z.K. and Wang, Z.G. (2001) *J. Appl. Polym. Sci.*, 82, 2739–2743.
9. Kim, J.T., Park, J.K. and Lee, D.C. (2002) *Polym. Int.*, 51, 1063–1065.
10. Lee, Y., Han, S., Lim, H., Jung, H. Cho, J. and Kim, Y. (2001) *J. Adhes. Sci. Technol.*, 15, 1079–1089.
11. Matyjaszewski, K. and Davis, T.P. Handbook of Radical Polymerization, John Wiley & Sons, Hoboken, 2002.
12. Jordan, R. and Ulman, A. (1998) *J. Am. Chem. Soc.*, 120, 243–247.
13. Ingall, M.D.K., Honeyman, C.H., Mercure, J.V., Bianconi, P.A. and Kunz, R.R. (1999) *J. Am. Chem. Soc.*, 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. and Hawker, C.J. (1999) *Macromolecules*, 32, 1424–1431.
15. Burkett, S.L., Ko, N., Stern, N.D., Caissie, J.A. and Sengupta, D. (2006) *Chem. Mater.*, 18, 5137–5143.
16. Baum, M. and Brittain, W.J. (2002) *Macromolecules*, 35, 610–615.
17. Xu, F.J., Li, Y.L., Kang, E.T. and Neoh, K.G. (2005) *Biomacromolecules*, 6, 1759–1768.
18. Edmondson, S., Osborne, V.L. and Huck, W.T.S. (2004) *Chem. Soc. Rev.*, 35, 14–22.
19. Liu, P. and Zhang, L.X. (2008) *J. Macromol. Sci., A*, 45, 17–21.
20. Li, X.D., Zhong, Z.X., Han, S.H., Lee, S.H. and Lee, M.H. (2005) *Polym. Int.*, 54, 406–411.
21. Cheng, Z., Zhu, X., Kang, E.T. and Neoh, K.G. (2006) *Macromolecules*, 39, 1660–1663.
22. Avram, E. (2001) *Polym.-Plast. Technol. Eng.*, 40, 275–281.
23. Xu, F.J., Zhao, J.P., Kang, E.T. and Neoh, K.G. (2007) *Ind. Eng. Chem. Res.*, 46, 4866–4873.
24. Xu, F.J., Zhao, J.P., Kang, E.T., Neoh, K.G. and Li, J. (2007)*Langmuir*, 23, 8585–8392.
25. Xu, F.J., Yuan, Z.L., Kang, E.T. and Neoh, K.G. (2004) *Langmuir*, 20, 8200–8208.
26. Moulder, J.F., Stickle, W.F., Sobol, P.E. and Bomben, K.D. Handbook of X-ray Photoelectron Spectroscopy, Perkin-Elmer, Eden Prairie, 1992.
27. Nishiyama, S., Goto, A., Saito, K., Sugita, K., Tanmada, M., Sugo, T., Funami, T., Goda, Y. and Fujimoto, S. (2002) *Anal. Chem.*, 74, 4933–4936.
28. Grano, V., Diano, N., Rossi, S., Portaccio, M., Attanasio, A., Cermola, M., Spiezie, R., Citton, C. and Mita, D.G. (2004) *Biotechnol. Prog.*, 20, 1393–1401.
29. Tan, K.L., Woon, L.L., Wong, H.K., Kang, E.T. and Neoh, K.G. (1993) *Macromolecules*, 26, 2832–2836.
30. Clark, D.T. and Dilks, A. (1979) *J. Polym. Sci. Polym. Chem. Ed.*, 17, 957–976.
31. Xu, F.J., Kang, E.T. and Neoh, K.G. (2005) *Macromolecules*, 38, 1573–1580.
32. Yoshikawa, C., Goto, A., Tsujii, Y., Fukuda, T., Kimura, T., Yamamoto, K. and Kishida, A. (2006) *Macromolecules*, 39, 2284–2290.