REFERENCES

1.Halperin A.; Tirrell M.; Lodge T. P. "Tethered chains in polymer microstructures" *Adv. Polym. Sci.* **1992**, 100, 31-71.

2. Jones R. A. L.; Richards R. W. "Polymers at surfaces and interfaces" Cambridge University Press, Cambridge, **1999**.

3. Mathauer, K.; Embs F.; Wegner, G. "Comprehensive Polymer Science, Vol. 1. Suppl" (Ed.: G. Allen), *Pergamon Press, Oxford,* **1992**, p. 449.

4. Decher, G. "Multilayer Thin Films. Sequential Assembly of Nanocomposite Materials" *Wiley-VCH, Weinheim* **2002**.

5. Caruso, F.; Furlong, D.N.; Ariga, K.; Ichinose, I.; Kunitake, T. "Characterization of polyelectrolyte-protein multilayer films by atomic force microscopy, scanning electron microscopy, and fourier transform infrared reflection-absorption spectroscopy" *Langmuir* **1998**, *14,* 4559-4565.

6. Krasemann, L.; Tieke. B.; "Composite membranes with ultrathin separation layer prepared by self-assembly of polyelectrolytes" *Mat. Sci. Eng.* **1999**, *C 8-9,* 513-518.

7. Wu, A.; Yoo, D.; Lee, J.K.; Rubner, M.F. "Solid-state light-emitting devices based on the tris-chelated ruthenium (II) complex: 3. high efficiency devices via a layer-by-layer molecular-level blending approach" *J. Am. Chem. Soc.* **1999**, *121*, 4883-4891.

8. Decher, G.; Hong, J.-D.; "Schmitt, J. Buildup of ultrathin multilayer films by a self-assembly process: III. Consecutively alternating adsorption of anionic and cationic polyelectrolytes on charged surfaces" *Thin Solid Films* **1992**, *210-211*, 831-835.

9. Schoeler, B.; Kumaraswamy, G.; Caruso, F. "Investigation of the influence of polyelectrolyte charge density on the growth of multilayer thin films prepared by the layer-by-layer technique" *Macromolecules* **2002**, *35*, 889-897.

10. Shiratori, S.S.; Rubner, M.F. "pH-Dependent thickness behavior of sequentially adsorbed layers of weak electrolytes" *Macromolecules* **2000,** *33*, 4213.

11. Lvov, Y.; Onda, M.; Ariga, K.; Kunitake, T. "Ultrathin flims of charged polysaccharides assembled alternately with linear polyions" *J. Biomater. Sci. Polymer Edn.* **1998,** *9*, 345-355.

12. Serizawa, T.; Yamaguchi, M.; Akashi, M. "Alternating bioactivity of polymeric layer-by-layer assemblies : anti-vs procoagulation of human blood on chitosan and dextran sulfate layers" *Biomacromolecules* **2002,** *3*, 724-731.

13. Harris, J. J.; Derose, P. M.; Bruening, M. L. "Synthesis of Passivating, Nylon Like Coatings through Cross-Linking of Ultrathin Polyelectrolyte Films" *J Am. Chem. Soc.* **1999**, *121*, 1978-1979.

14. Nagal, M.; Kim, B. Y.; Bruening, M. L. "Ultrathin, Hyperbranched Poly(acrylic acid) Membranes on Porous Alumina Supports" *J Am. Chem. Soc.* **2000,** *122*, 11670-11678.

15. Ansell, M. A.; Cogan, E. B.; Page, C. "Coordinate Covalent Cobalt-Diisocyanide Multilayer Thin Films Grown One Molecular Layer at a Time" *J. Langmuir* **2000,** *16*, 1172-1179.

16. Serizawa, T.; Nanameki, K.; Yamamoto, K.; Akashi, M. "Thermoresponsive Ultrathin Hydrogels Prepared by Sequential Chemical Reactions" *Macromolecules* **2002,** *35*, 2184-2189.

17. Yang, S. U.; Lee, D.; Cohen, R. E.; Rubner, M. F. "Bioinert Solution-Cross-Linked Hydrogen-Bonded Multilayers on Colloidal Particles" *Langmuir* **2004,** *20,* 5978-5981.

18. Van der Steeg, H. G. M.; Cohen Stuart, M. A.; de Keizer, A. Bijsterbosch, B. H. "Polyelectrolyte adsorption: a subtle balance of forces" *Langmuir* **1992,** *8,* 2538-2546.

19. Cohen Stuart, M. A. "Polyelectrolyte adsorption" *J. Phys. (France)* **1988**, *49*, 1001-1008.

20. Decher, G.; Hong, J. D. "Buildup of ultrathin multilayer films by a self-assembly process. 1. Consecutive adsorption of anionic and cationic bipolar amphiphiles on charged surfaces" *Makromol. Chem. Makomol. Symp.* **1991**, *46,* 321-327.

21. Zhang, H.; Rühe, J. " Interaction of strong polyelectrolytes with surface-attacted polyelectrolyte brushes polymer brushes as substrates for the layer-by-layer deposition of polyelectrolyte" *Macromolecules* **2003,** *36,* 6593-6598.

22. Zhang, H.; Rühe, J. "Weak Polyelectrolyte Brushes as Substrates for the Formation of Surface-Attached Polyelectrolyte-Polyelectrolyt Complexes and Polyelectrolyte Multilayers" *Macromolecules* **2005,** *38,* 10743-10749.

23. Zhao, B.; Brittain, W. J. "Polymer Brushes: Surface-Immobilized Macromolecules" *Prog. Polym. Sci.* **2000**, *25,* 677-710.

24. Raphael, E.; De Gennes, P. G. "Rubber-Rubber Adhesion with Connector Molecules" *J. Phys Chem* **1992**, *96,* 4002-4007.

25. Ji, H.; De Gennes, P. G. "Adhesion via Connector Molecules: The Many-Stitch Problem" *Macromolecules* **1993**, *26,* 520-525.

26. Amiji, M.; Park, K. J. "Surface Modification of Polymeric Biomaterials with Poly(ethylene oxide), Albumin, and Heparin for Reduced Thrombogenicity" *Biomater. Sci. Polym. Ed.* **1993**, *4*, 217-234.

27. Van Zanten, J. H. "Terminally Anchored Chain Interphases: Their Chromatographic Properties" *Macromolecules* **1994**, *27*, 6797-6807.

28. Joanny, J. F. "Lubrication by Molten Polymer Brushes" *Langmuir* **1992**, *8*, 989-995.

29. Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. "Dynamic Contact Angle Measurement of Temperature-Responsive Surface Properties for Poly(N-isopropylacrylamide) Grafted Surfaces" *Macromolecules* **1994,** *27*, 6163-6166.

30. Ito, Y.; Ochiai, Y.; Park, Y. S.; Imanishi, Y. "pH-Sensitive Gating by Conformational Change of a Polypeptide Brush Grafted onto a Porous Polymer Membrane" *J. Am. Chem. Soc.* **1997**, *119*, 1619-1623.

31. Ito, Y.; Park, Y. S.; Imanishi, Y. "Visualization of Critical pH-Controlled Gating of a Porous Membrane Grafted with Polyelectrolyte Brushes" *J. Am. Chem. Soc.* **1997**, *119*, 2739-2740.

32. Ito, Y.; Nishi, S.; Park, Y. S.; Imanish, Y. "Oxidoreduction-Sensitive Control of Water Permeation through a Polymer Brushes-Grafted Porous Membrane" *Macromolecules* **1997**, *30*, 5856-5859.

33. Velten, U.; Shelden, R. A.; Caseri, W. R.; Suter, U. W.; Li, Y. "Polymerization of Styrene with Peroxide Initiator Ionically Bound to High Surface Area Mica" *Macromolecules* **1999**, *32*, 3590-3597.

34. Velten, U.; Tossati, S.; Shelden, R. A.; Caseri, W. R.; Suter, U. W.; Hermann, R.; Müller, M. "Graft Polymerization of Styrene on Mica: Formation and Behavior of Molecular Droplets and Thin Films" *Langmuir* **1999**, *15*, 6940-6945.

35. Niu, Q. J.; Fréchet, J. M. J. "Polymers for 193-nm Microlithography: Regioregular 2-Alkoxycarbonylnortricyclene Polymers by Controlled Cyclopolymerization of Bulky Ester Derivatives of Norbornadiene" *Angew Chem, Int Ed Engl* **1998**, *37*, 667-670.

36. Singhvi, R.; Kumar, A.; Lopez, G. P.; Stephanopoulos, G. N.; Wang, D. I. C.; Whitesides, G. M.; Ingber, D. E. "Engineering Cell-Shape and Function" *Science* **1994**, *264*, 696-698.

37. Chen, C. S.; Mrksich, M.; Huang, S.; Whitesides, G. M.; Ingber, D. E. "Geometric Control of Cell Life and Death" *Science* **1997**, *276*, 1425-1428.

38. Aksay, I. A.; Trau, M.; Manne, S.; Honma, I.; Yao, N.; Zhou, L.; Fenter, P.; Eisenberger, P. M.; Gruner, S. M. "Biomimetic Pathways for Assembling Inorganic Thin Films" *Science* **1996**, *273*, 892-898.

39. Balazs, A. C.; Singh, C.; Zhulina, E.; Gersappe, D.; Pickett, G. "Patterned Polymer Films" *MRS Bull* **1997**, *22*, 16-21.

40. Soga, K. G.; Zuckermann, M. J.; Guo, H. "Binary Polymer Brush in a Solvent" *Macromolecules* **1996**, *29*, 1998-2005.

41. Mansky, P.; Liu, Y.; Huang, E.; Russell T. P.; Hawker, C. "Controlling Polymer-Surface Interactions with Random Copolymer Brushes" *Science* **1997**, *275*, 1458-1460.

42. Zhao, B.; Brittain, W. J. "Synthesis of Tethered Polystyrene-block-Poly (methyl methacrylate) Monolayer on a Silicate Substrate by Sequential Carbocationic Polymerization and Atom Transfer Radical Polymerization" *J. Am. Chem. Soc.* **1999**, *1219*, 3557-3558.

43. Nakayama, Y.; Matsuda, T. "Surface Macromolecular Architectural Designs Using Photo-Graft Copolymerization Based on Photochemistry of

Benzyl N,N-Diethyldithiocarbamate" *Macromolecules* **1996**, *29*, 8622-8630.

44. Ejaz, M.; Yamamoto, S.; Ohno, K.; Tsujii, Y.; Fukuda, T. "Controlled Graft Polymerization of Methyl Methacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques" *Macromolecules* **1998**, *31*, 5934-5936.

45. Husseman, M.; Malmström, E. E.; McNamara, M.; Mate, M.; Mecerreyes, D.; Benoit, D. G.; Hedrick, Mansky, P.; Huang, E. ; Russell, T. P.; Hawker, C. J. "Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques" *Macromolecules* **1999**, *32*, 1424-1431.

46. Huang, X.; Wirth, M. J. "Surface Initiation of Living Radical Polymerization for Growth of Tethered Chains of Low Polydispersity" *Macromolecules* **1999**, *32*, 1694-1696.

47. Sedjo, R. A.; Mirous, B. K.; Brittain, W. J. "Synthesis of Polystyrene-block-poly(methyl methacrylate) Brushes by Reverse Atom Transfer Radical Polymerization" *Macromolecules* **2000**, *33*, 1492-1493.

48. de Boer, B.; Simon, H. K.; Werts, M. P. L.; van der Vegte, E. W.; Hadziioannou, G. ""Living" Free Radical Photopolymerization Initiated from Surface-Grafted Iniferter Monolayers" *Macromolecules* **2000**, *33*, 349-356.

49. Ejaz, M.; Yamamoto, K.; Ohno, Y. T.; Fukuda, T. "Controlled Graft Polymerization of Mrthyl Mathacrylate on Silicon Substrate by the Combined Use of the Langmuir-Blodgett and Atom Transfer Radical Polymerization Techniques" *Macromolecule* **1998**, *31*, 5934-5936.

50. Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. "Polymers at Interfaces: Using Atom Transfer Radical

Polymerization in the Controlled Growth of Homopolymers and Block Copolymers from Silicon Surfaces in the Absence of Untethered Sacrificial Initiator" *Macromolecules* **1999**, *32*, 8716-8724.

51. *von* Werene, T.; Patten, T.E. "Atom Transfer Radical Polymerization from Nanoparticles: A Tool for the Preparation of Well-defined Hybrid Nanostructures and for Understanding the Chemistry of Controlled/"Living" Radical Polymerizations from Surfaces" *J. Am. Chem. Soc.* **2001**, *123*, 7497-7505.

52. Szwarc, M.; Levy, M.; Milkovich, R. "Polymerization Initiated by Electron Transfer to Monomer a New Method of Formation of Block Polymers" *J. Am. Chem. Soc.* **1956**, *78*, 2656-2657.

53. Flory, P. J. "Principles of Polymer Chemistry" *Cornell Uni. Press*, Ithaca, NY. **1978**.

54. Webster, O. W. "Living Polymerization Methods" *Science* **1991**, *251*, 887-.

55. Moad, G.; Rizzardo, E.; Solomon D. H. "Selectivity of the Reaction of Free Radicals with Styrene" *Macromolecules* **1982**, *15*, 909-914.

56. Georges, M. K.; Veregin, R. P. N.; Kazmaier, P. M.; Hamer, G. K. "Narrow Molecular Weight Resins by a Free-Radical Polymerization Process" *Macromolecules* **1993**, *26*, 2987-2988.

57. Kato, M.; Kamigaito, M.; Sawamoto, M.; Higashimura, T. "Polymerization of Methyl Methacrylate with the Carbon Tetrachloride/ Dichlorotris-(triphenylphosphine)ruthenium(II)/Methylaluminum Bis(2,6-di-*tert*-butylphenoxide) Initiating System: Possibility of Living Radical Polymerization" *Macromolecules* **1995**, *28*, 1721-1723.

58. Wang, J. S.; Matyjaszewski, K. "Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexs" *J. Am. Chem. Soc.* **1995**, *117*, 5614-5615.

59. Percec, V.; Barboiu, B. ""Living" Radical Polymerization of Styrene Initiated by Arenesulfonyl Chlorides and CuI(bpy)nCl" *Macromolecules* **1995**, *28*, 7970-7972.

60. Wayland, B. B.; Poszmik, G.; Mukerjee, S. L.; Fryd, M. "Living Radical Polymerization of Acrylates by Organocobalt Porphyrin Complexes" *J. Am. Chem. Soc.* **1994**, *116*, 7943-7944.

61. Granel, C.; DuBois, P.; Jerome, R.; Teyssie, P. "Controlled Radical Polymerization of Methacrylic Monomers in the Presence of a Bis(ortho-chelated) Arylnickel(II) Complex and Different Activated Alkyl Halides" *Macromolecules* **1996**, *29*, 8576-8582.

62. Matyjaszewski, K. "Controlled Radical Polymerization" *ACS Symposium Series NO. 685 American Chemical Society:* Washington, DC, **1997.**

63. Matyjaszewski, K. "Mechanistic and Synthetic Aspects of Atom Transfer Radical Polymerization" *J. Macromol. Sci., Pure Appl. Chem.* **1997**, *A34*, 1785-1801.

64. Chambard, G.; Klumperman, B.; German, A. L. "Effect of Solvent on the Activation Rate Parameters for Polystyrene and Poly(butyl acrylate) Macroinitiators in Atom Transfer Radical Polymerization" *Macromolecules* **2000**, *33*, 4417-4421.

65. Matyjaszewski, K.; Xia, J. "Atom Transfer Radical Polymerization" *Chem. Rev.* **2001**, *101*, 2921-2990.

66. Matyjaszewski, K.; Xia, J. "Controlled/"Living" Radical Polymerization. Atom Transfer Radical Polymerization Using Multidentate Amine Ligands" *Macromolecules* **1997**, *30*, 7697-7700.

67. Suzuki, K.; Siddiqui, S.; Chappell, C.; Siddiqui, J.A.; Ottenbrite, R. M. "Modification of porous silica particles with poly(acrylic acid)" *Polym. Adv. Technol.* **2000**, *11*, 92-97.

68. Shi, Y.; Seliskar, C. "Optically Transparent Polyelectrolyte-silica Composite Materials: Preparation, Characterization, and Application in Optical Chemical Sensing" *J. Chem. Mater.* **1997**, *9*, 821-829.

69. Shimomura, M.; Kikuchi, H.; Matsumoto, H.; Yamauchi, T.; Miyauchi, S. *Polym.J.(Tokyo)* **1995**, *27*, 974.

70. Yoshinaga, K.; Kondo, K.; Kondo, A. "Capabilities of polymer-modified monodisperse colloidal silica particles as biomaterial carrier" *Colloid Polym. Sci.* **1997**, *275*, 220.

71. Davis, K.A.; Matyjaszewski, K. "Atom Transfer Radical Polymerization of tert-butyl acrylate and Preparation of Block Copolymers" *Macromolecules* **2000**, *33*, 4039–4047.

72. Davis, K. A.; Charleux, B.; Matyjaszewski, K. "Preparation of Block Copolymers of Polystyrene and Poly(t-butyl acrylate) of various Molecular weights and Architectures by Atom Transfer Radical Polymerization" *J Polym Sci, Part A: Polym Chem* **2000**, *38*, 2274–2283.

73. Boyes, S. G.; Akgun, B.; Brittain, W. J.; Foster, M. D. "Synthesis, Characterization, and Properties of Polyelectrolyte Block Copolymer Brushes Prepared by Atom Transfer Radical Polymerization and Their Use in the Synthesis of Metal Nanoparticles" *Macromolecules* **2003**, *36*, 9539-9548.

74. Roberts, G.A.F., Muzzarelli, R. A. A., Peter, M. G., Eds. "In Chitin Handbook" *Italy, Atec Edizioni* **1997.**

75. Inoue, Y., Eds. "In Chitin Handbook" *Italy, Atec Edizioni* **1997.**

76. Roberts, G.A.F., Eds. "In Chitin and Chitosan Handbook" *Italy, Atec Edizioni* **1997**.

77. Potisatityuenyong, A.; Tumcharern, G.; Dubas, S. T.; Sukwattanasinitt, M. "Layer-by-layer assembly of intact polydiacetylene vesicles with retained chromic properties" *Journal of Colloid and Interface Science* **2006**, *304*, 45-51.

78. Seymour, M. P. "Introduction to Polymers Chemistry" *Tokyo, McGraw-Hill Kogakusha* **1971**

79. www.uta.edu/optics/research/ellipsometry/ellipsometry.htm

80. Xiao, S. J. "Tailored Organic Thin Films on Gold and Titanium: Peptide-Grafting, Protein Resistance and Physical Characterization" *Thesis; M. Sc. Chemistry, Fudan University, Shanghai China* **1999**.7

81. www.chembio.uoguelph.ca/educmat/chm729/afm/introdn.htm

82. Seong, H-S.; Whang, H. S.; Ko, S-W. "Synthesis of a Quaternary Ammonium Derivative of Chitooligosaccharide as Antimicrobial Agent for Celluulosic Fibers" *J. Appl. Polym. Sci.* **2000**, *76*, 2009-2015.

83. Marutani, E.; Yamamoto, S.; Ninjbadgar, T.; Tsujii, Y.; Fukuda, T.; Takano, M. "Surface-initiated Atom Transfer Radical Polymerization of methyl Methacrylate on magnetite nanoparticles" *Polymer* **2004**, 45, 2231-2235.

84. 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. "Controlled Synthesis of Polymer Brushes by "Living" Free Radical Polymerization Techniques" *Macromolecules* **1999**, *32*, 1424-1431.

85. Akkahat, P. *Attachment of biotin on silicon surface-tethered poly(acrylic acid) brushes*. Master's Thesis, Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University, **2006.**

APPENDICES

APPENDIX A

Proton nuclear magnetic resonance (^{1}H NMR) spectra

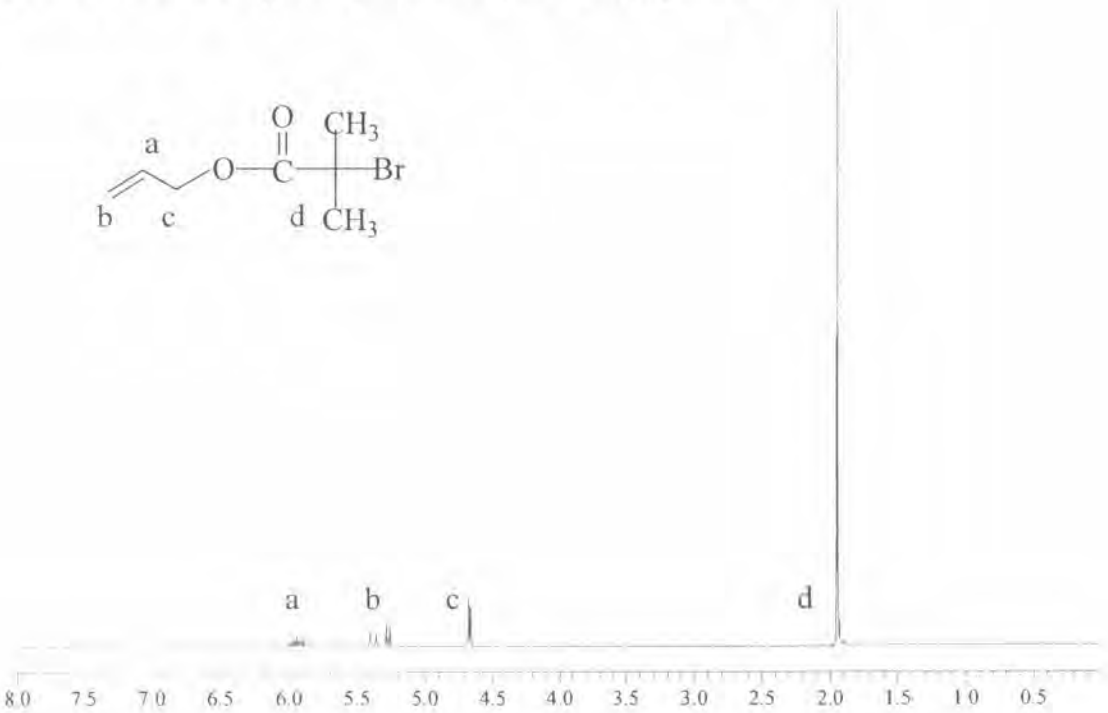


Figure A-1 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2-bromo-2-methylpropionic acid allyl ester **(1)**

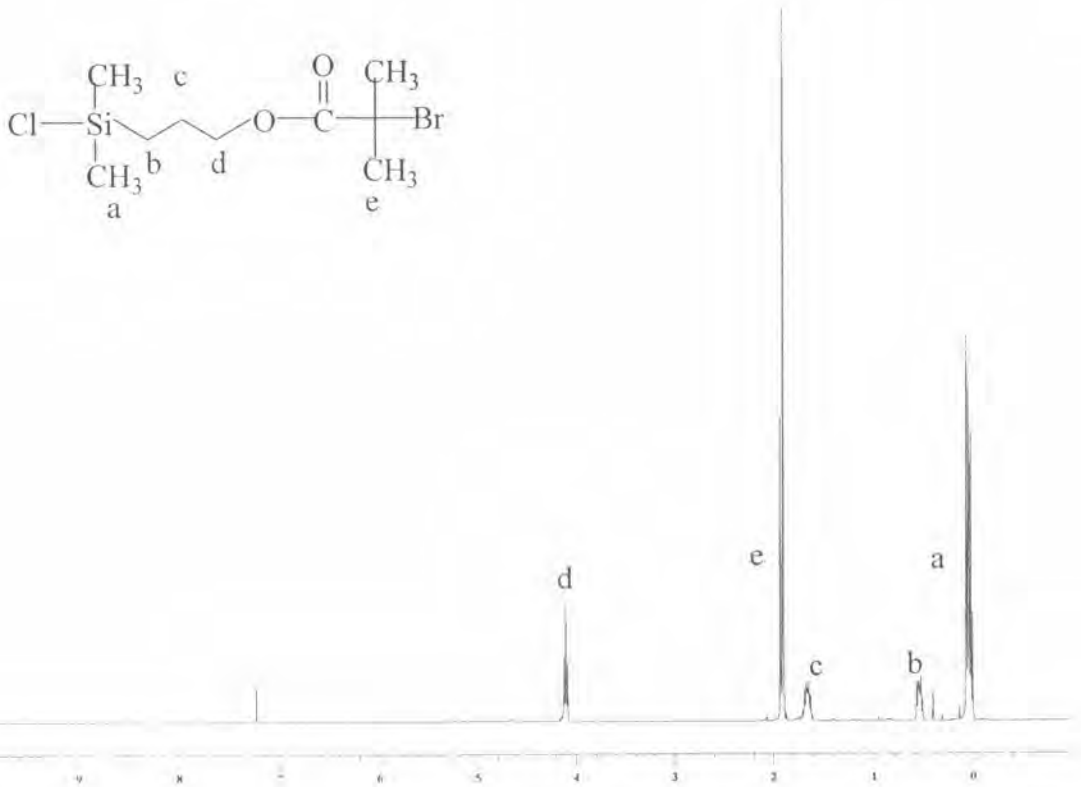


Figure A-2 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2-bromo-2-methylpropionic acid 3-(dimethylchloro silanyl) propyl ester **(2)**

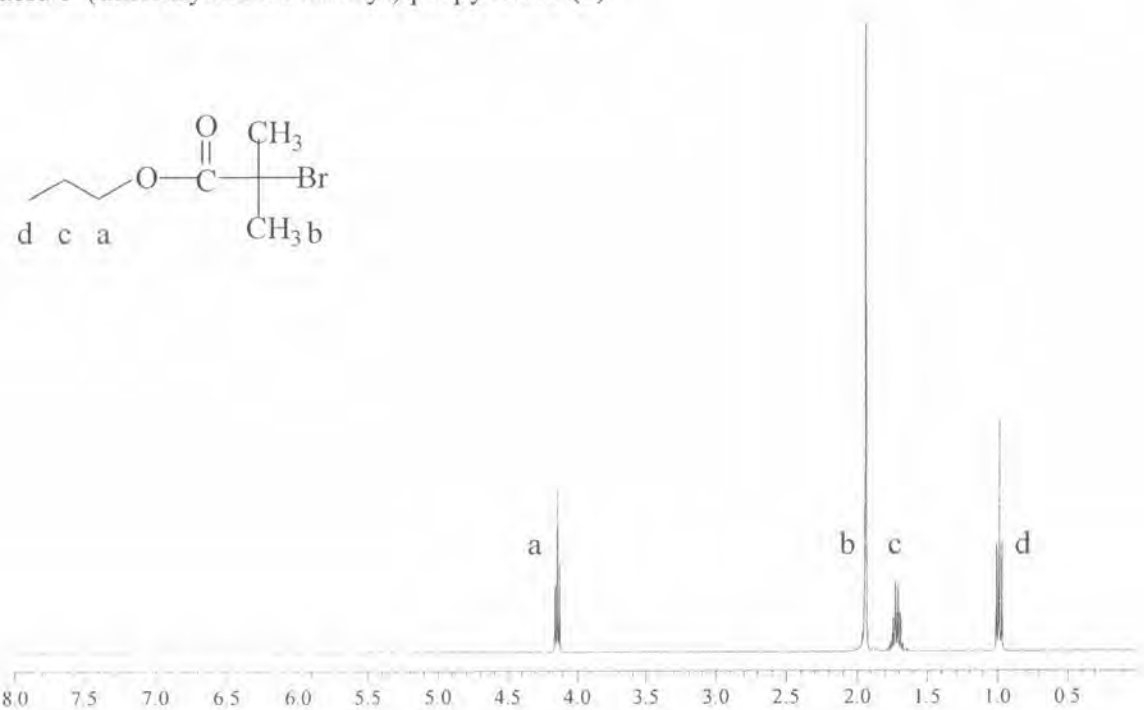


Figure A-3 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of 2-bromo-2-methylpropionic acid propyl ester **(3)**

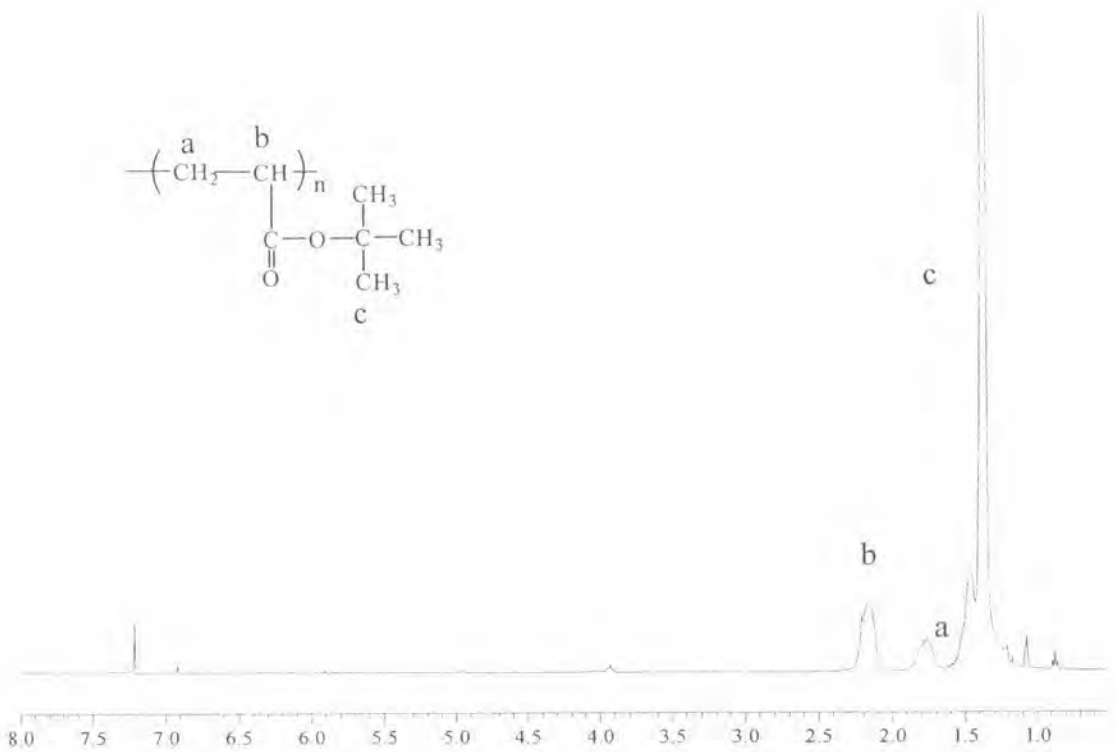


Figure A-4 ^{1}H-NMR spectrum (400 MHz, $CDCl_3$) of P*t*-BA

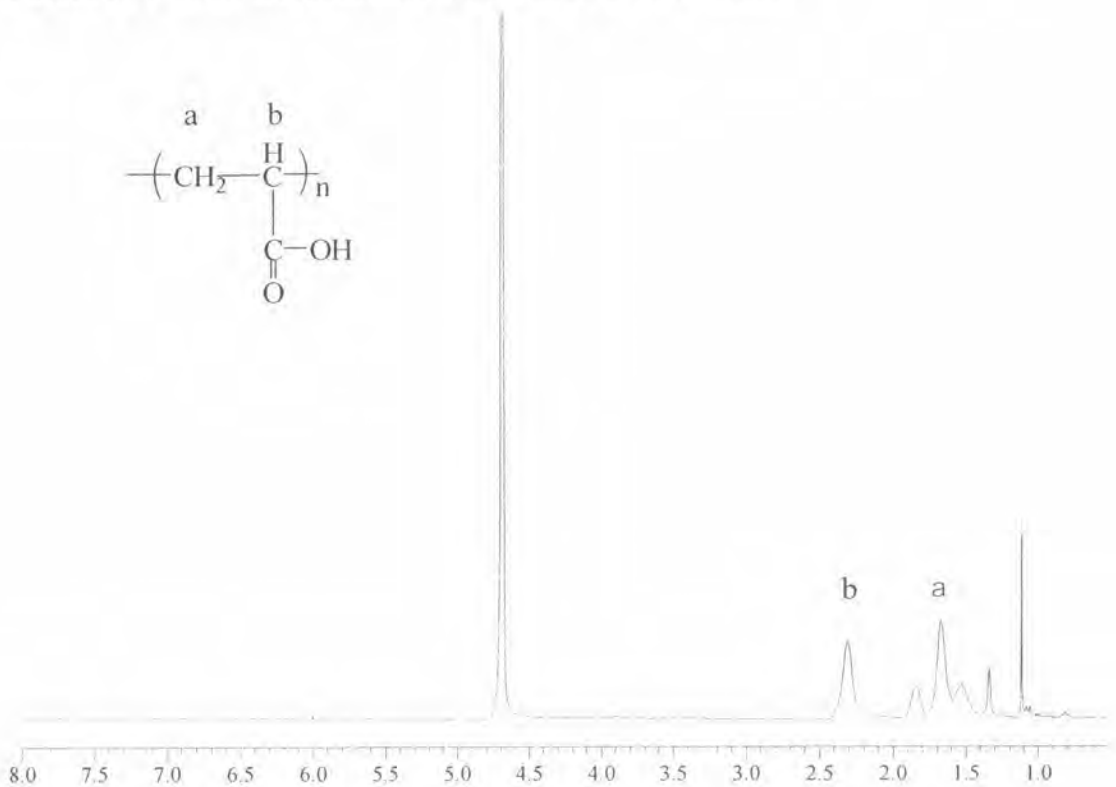


Figure A-5 The ^{1}H-NMR spectrum (400 MHz, D_2O) of PAA

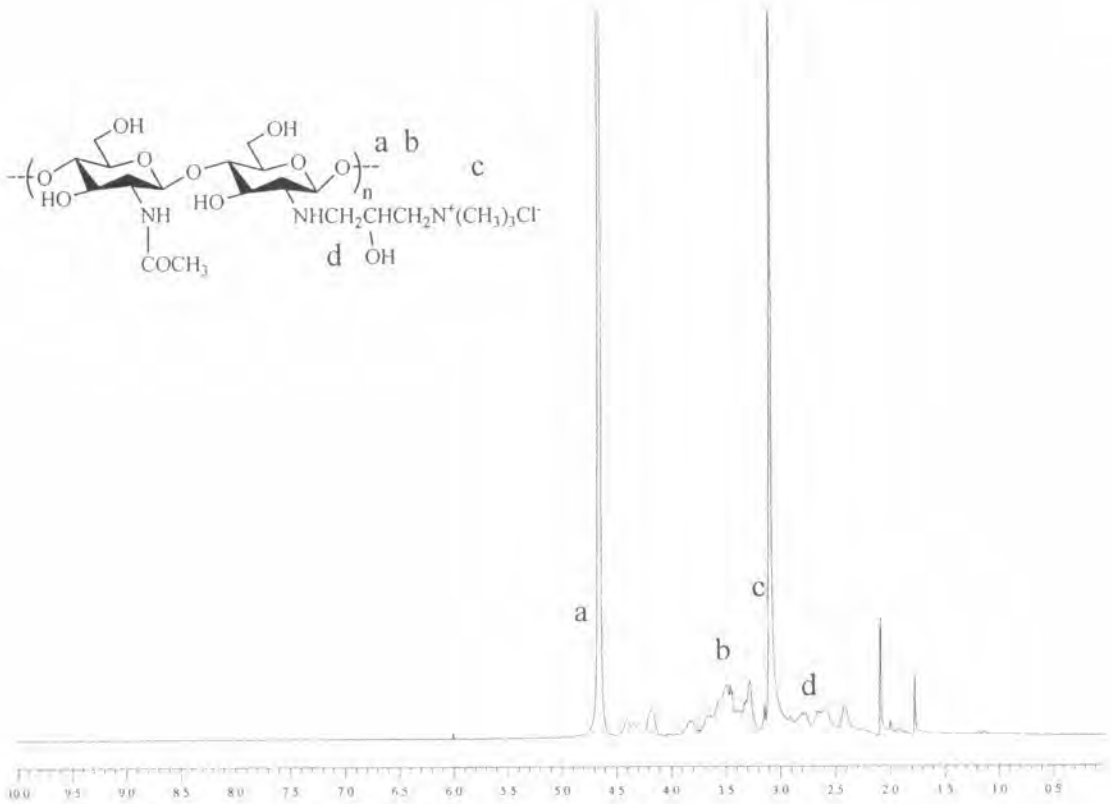


Figure A-6 ^{1}H-NMR spectrum (400 MHz, D_2O) of HTACC

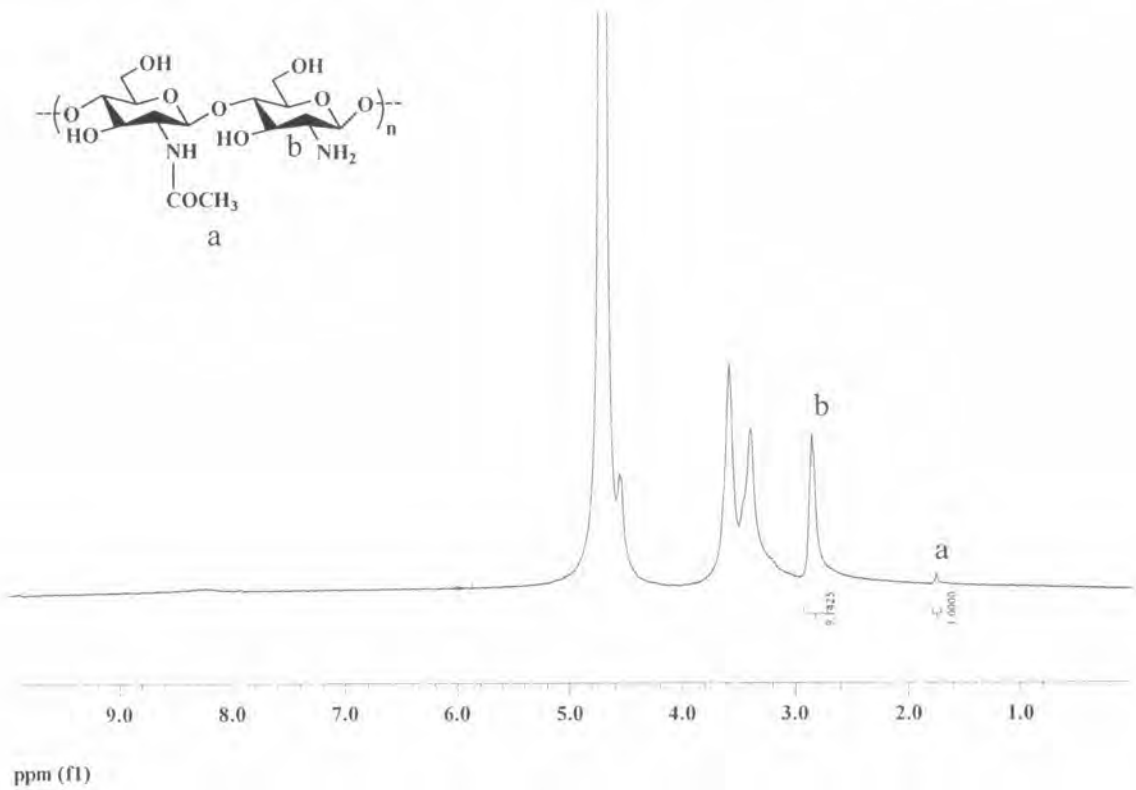


Figure A-7 ^{1}H-NMR spectrum (400 MHz, D_2O) of Chitosan $\overline{M}_w$ 100,000, 96% DD

Table A-1 Information from ^{1}H NMR spectrum of chitosan used in this study

	δ (ppm)	**Integration**	**Relative Amount of units**
-C<u>H</u>NH$_2$ of GlcN	2.80	9.1	9.1/1
-C<u>H</u>$_3$ of GlcNAc	1.75	1.0	1.0/3

Considering the total repeating units in chitosan as 100%, %DD of 96 % was calculated based on the data in Table 4.2 using the following equation.

$$\%DD = \frac{\text{Amount of GlcN unit in chitosan}}{\text{The total amount of GlcN and GlcNAc units in chitosan}} \times 100$$

$$= \frac{(9.1/1)}{(1.0/3) + (9.1/1)} \times 100\% = 96\ \%$$

APPENDIX B

B. Data corresponding to the plots in Chapter IV

Table B-1 Average molecular weight and molecular weight distribution of P*t*-BA brushes analyzed by GPC as a function of time (DP =100, 200)

Time (h)	GPC data					
	DP 100			DP 200		
	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$	$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
3	1990	2157	1.10	3058	3302	1.08
6	3869	4063	1.05	5499	5992	1.09
12	6834	7309	1.07	11765	12467	1.06
24	11965	12563	1.05	22101	24976	1.13

Table B-2 The thickness of linear P*t*-BA brushes calculated from ellipsometric data as a function of average molecular weight of P*t*-BA (DP = 100)

Time (h)	Thickness (nm)	GPC data (DP 100)		
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
3	NA	2047	2251	1.10
6	3.11	4592	4816	1.05
12	4.47	6612	7273	1.10
24	6.86	12237	13338	1.09

Table B-3 The thickness of linear P*t*-BA brushes calculated from ellipsometric data as a function of average molecular weight of P*t*-BA (DP = 200)

Time (h)	Thickness (nm)	GPC data (DP 200)		
		$\overline{M}_n$	$\overline{M}_w$	$\overline{M}_w/\overline{M}_n$
3	2.70	3058	3302	1.08
6	4.21	5769	6345	1.10
12	7.27	12465	13586	1.09
24	10.20	20101	21307	1.06

Table B-4 Advancing (θ_A) and receding (θ_R) water contact angles of P*t*-BA (DP = 100, 200) as a function of time

Time (h)	DP =100		DP = 200	
	θ_A (°)	θ_R (°)	θ_A (°)	θ_R (°)
0[a]	68 ± 2.4	56 ± 2.2	67 ± 2.2	58 ± 2.0
3	75 ± 2.1	66 ± 2.5	75 ± 2.1	67 ± 1.7
6	77 ± 1.7	71 ± 2.2	83 ± 1.7	69 ± 2.4
12	85 ± 1.5	78 ± 1.9	86 ± 2.1	75 ± 2.1
24	89 ± 2.0	80 ± 1.8	92 ± 1.8	80 ± 2.2

[a] is advancing and receding water contact angle of α-bromoisobutylyl ester initiator on silicon surface.

Table B-5 UV-Vis absorbance at 640 nm of CHI/ PPCDA vesicles multilayer ($\overline{M}_n$ of CHI =100,000 g/mole) on glass-tethered PAA brushes having $\overline{M}_n$ = 9125 and 12661 as a function of number of layer

Number of layers	UV-Vis absorbance at 640 nm	
	$\overline{M}_n$ = 9125	$\overline{M}_n$ = 12661
6	0.045	0.086
8	0.084	0.161
10	0.091	0.171
12	0.110	0.154
14	0.120	0.169
16	0.169	0.219

Table B-6 UV-Vis absorbance at 640 nm of a bilayer CHI/PPCDA vesicles ($\overline{M}_n$ of CHI = 743,000 g/mole) on glass-tethered PAA brushes having $\overline{M}_n$ = 8343 and 11760 as a function of deposition time

Deposition Time (min)	UV-Vis absorbance at 640 nm	
	$\overline{M}_n$ = 8343	$\overline{M}_n$ = 11760
5	0.25	0.34
10	0.29	-
15	-	0.5
20	0.36	0.62
30	-	0.91

Table B-7 Ellipsometric thickness of CHI/PAA multilayer on silicon-tethered PAA brushes having $\overline{M}_n = 24,797$ and 13,835 as a function of number of layer

Number of layers	Thickness (nm)	
	$\overline{M}_n$ = **13,835**	$\overline{M}_n$ = **24,797**
0	6.70 ± 1.81	10.37 ± 0.92
1	9.95 ± 0.55	13.80 ± 1.55
2	11.90 ± 0.47	18.00 ± 0.87
3	20.98 ± 1.57	36.00 ± 1.57
4	28.65 ± 1.06	47.00 ± 1.06
5	36.78 ± 2.80	52.00 ± 2.80
6	42.34 ± 2.37	66.00 ± 2.37
7	51.00 ± 1.88	76.00 ± 1.88
8	55.30 ± 2.43	88.00 ± 2.22
9	54.97 ± 2.08	91.90 ± 1.90

Table B-8 Water contact angle of CHI/PAA multilayer on surface-tethered PAA brushes

Number of layer	Water contact angle (degree)
0	39 ± 1.1
1	57 ± 1.0
2	44 ± 3.1
3	54 ± 4.4
4	42 ± 1.0
5	54 ± 1.8
6	42 ± 1.5
7	62 ± 4.4
8	45 ± 0.9
9	58 ± 1.6
10	46 ± 1.4
11	55 ± 4.5

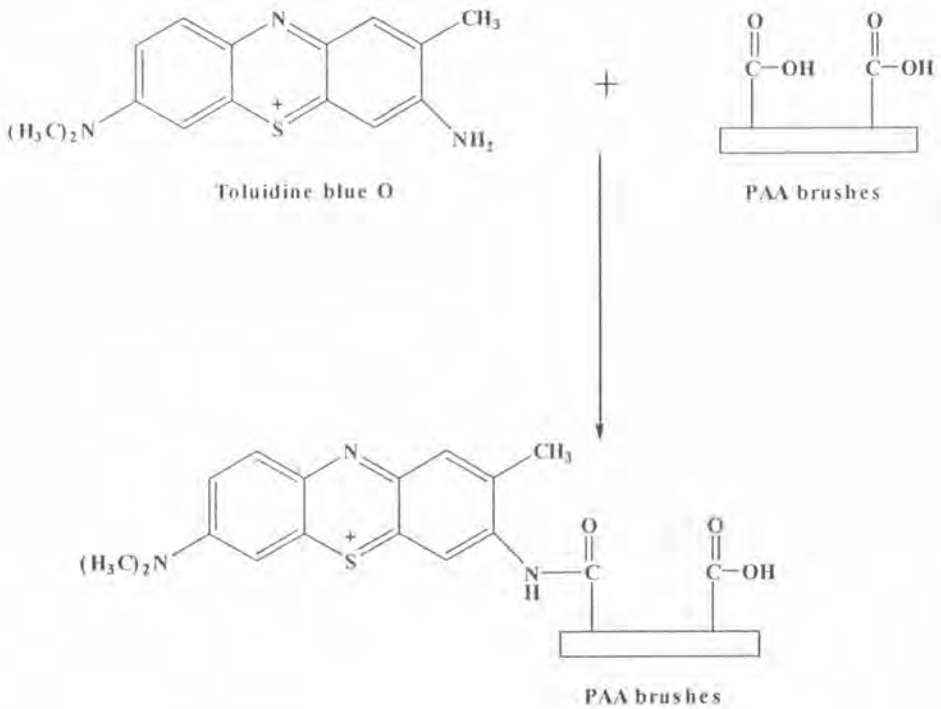
Table B-9 Amount of adsorbed albumin on CHI/PAA multilayer on PAA brushes having $\overline{M}_n$ = 11,092 and 18,202

Samples	Adsorped protein (µg/cm2) of Mutilayer film on PAA brushes substrate	
	$\overline{M}$ **n = 11,092**	$\overline{M}$ **n = 18,202**
PAA brushes	0.38 ± 0.15	0.45 ± 0.15
CHI	0.71 ± 0.14	0.88 ± 0.12
CHI/PAA	0.64 ± 0.31	0.76 ± 0.49
(CHI/PAA)CHI	0.80 ± 0.19	0.86 ± 0.34
(CHI/PAA)2	1.23 ± 0.31	1.82 ± 0.40
(CHI/PAA)2CHI	1.46 ± 0.27	1.98 ± 0.48

APPENDIX C

C-1 Toluidine blue O assay

Toluidine blue O assay is a method used for determination of the amount of carboxyl groups. The carboxyl groups of PAA brushes can form a complex with toluidine blue o. The absorbance of the solution containing the desorbed complex was measured at 633 nm. The COOH content was obtained from a calibration plot of the optical density versus dye concentration which is displayed in Figure C-2.



Scheme C-1 Formation of toluidine blue O complex with carboxyl group

Table C-1 Standard Toluidine blue O solution for the calibration curve.

Standard	Solution pH 10 (mL)	NaOH pH 10 (mL)	Toluidine blue O conc (mM)
S_1	1.00 toluidine blue O (0.5 mM)	9.00	0.0500
S_2	8.00 of S_1	2.00	0.0400
S_3	7.50 of S_2	2.50	0.0300
S_4	6.70 of S_3	3.20	0.0200
S_5	5.00 of S_4	5.00	0.0100
S_6	7.50 of S_5	2.50	0.0075
S_7	1.00 of S_6	9.00	0.0050
S_8	0.00 of S_7	10.00	0.0000

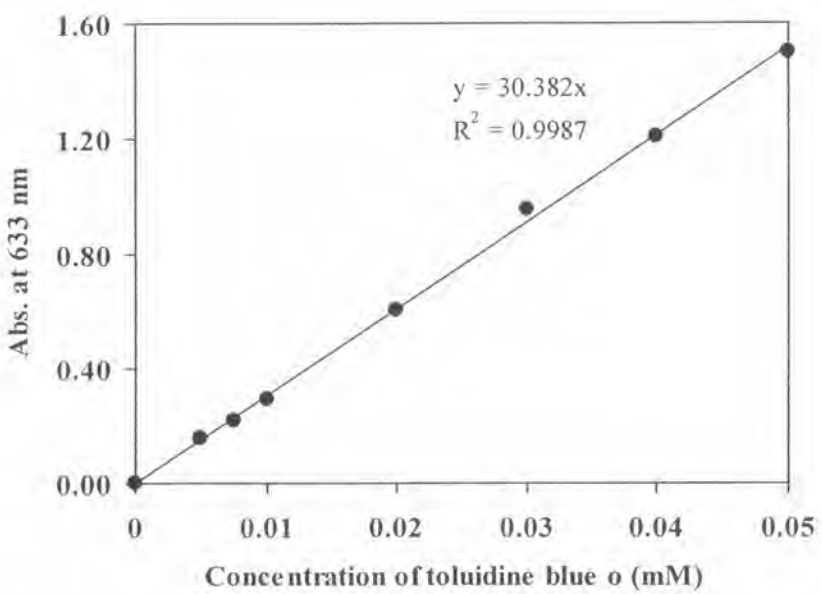
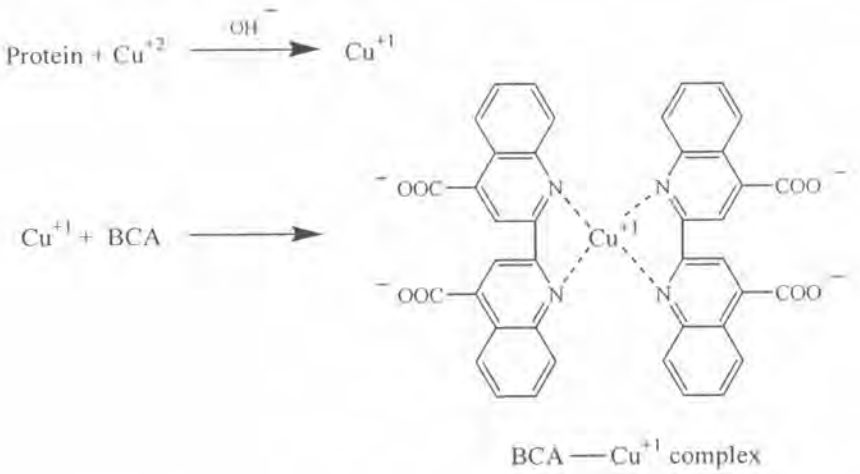


Figure C-1 Calibration curve of UV-Vis absorbance as a function of toluidine blue O concentration

C-2 Bicinchoninic acid assay

Bicinchoninic acid assay is a method used for determination of the amount of proteins. The standard reagents used in this method are reagent A, reagent B and reagent C. Reagent A consists of an aqueous solution of Na_2tartrate, Na_2CO_3, $NaHCO_3$ in 0.2 M NaOH, pH 11.25. Reagent B is 4% (W/V) bicinchoninic acid solution, pH 8.5. Reagent C is 4% $CuSO_4 5H_2O$ in deionized water.

The principle of the bicinchoninic assay (BCA) relies on the formation of a Cu^{2+}-protein complex under alkaline conditions, followed by reduction of the Cu^{2+} to Cu^{1+}. The amount of reduction is proportional to protein present. It has been shown that the peptide bond is able to reduce Cu^{2+} to Cu^{1+}. BCA forms a purple-blue complex with Cu^{1+} in alkaline environments, thus providing a basis to monitor the reduction of alkaline Cu^{2+} by proteins.[30] Figure B-1 shows complexation between bicinchoninic acid and Cu^{1+}.



Scheme C-2. Formation of purple complex between BCA and cuprous ion generated from the biuret reaction.

Calculation of Protein Adsorption

Table C-2 Standard BSA solution for the calibration curve.

Standard	Solution (mL)	SDS (mL)	BSA conc
S_1	0.25 of BSA (1000 (μg/mL)[a]	4.75	50
S_2	2.0 of S_1	3.00	20
S_3	2.5 of S_2	2.5	10
S_4	2.5 of S_3	2.5	5
S_5	0.5 of S_4	4.5	0.5
S_6	-	5.0	0.0

a : standard BSA was pipette from 1 mg/mL ampule

After reading the UV absorbance of standard BSA solution at λ = 562 nm, a calibration curve between UV absorbance versus standard BSA solution can be plotted (Figure B-2).

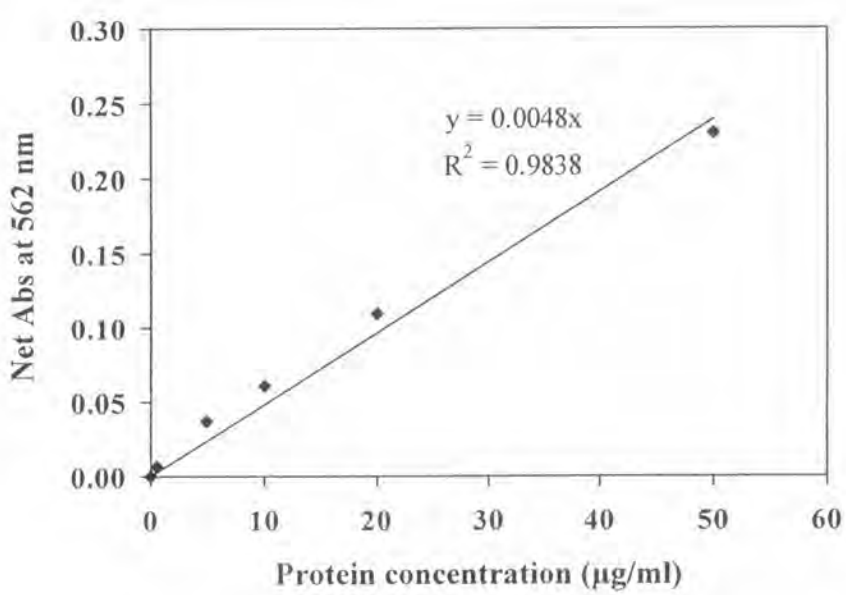


Figure C-2 Calibration curve of the amount of albumin and the absorbance obtained from BCA microassay.

The total amount of protein (P) in the original solution (2 mL) was calculated from the sampling sample (100 μL) + BCA working solution (100 μL) The protein concentration (C; μg/mL) in each well was determined from the calibration curve.

Table C-3 UV absorbance at λ_{562}, measured from sampling solution of various outermost layer

Samples	$N_{net}A_{562}$
PAA brushes $\overline{M}$ n 22391	0.006
(CHI/PAA)2	0.007
(CHI/PAA)2 CHI	0.013
(CHI/PAA)2 HTACC	0.008
(CHI/PAA)2 CHI/heparin	0.005

Net Absorbance at 562 nm ($N_{net}A_{562}$) = A_{562} sample – A_{562}blank C-1

$$\text{Total amount of protein (P)} = \frac{\text{C (μg/mL) x 100 (μL)}}{\text{1000 (μL/mL)}} \times \frac{\text{1000 (μL)}}{\text{100 (μL)}} \quad \text{C-2}$$

Adsorbed protein/surface area P_{ads} = P/surface area (2 sides) (μg/cm^2) C-3

Example: (CHI/PAA)$_2$ CHI which have $N_{net}A_{562}$ 0.013 Abs. so equal 2.66 μg/mL

From C-2 *Eq.* $P = \frac{\text{C (μg/mL) x 100 (μL)}}{\text{1000 (μL/mL)}} \times \frac{\text{1000 (μL)}}{\text{100 (μL)}}$

$= \frac{\text{2.66 (μg/mL) x 100 (μL)}}{\text{1000 (μL/mL)}} \times \frac{\text{1000 (μL)}}{\text{100 (μL)}}$

$= 2.66$ μg

From C-3 *Eq.* P_{ads} = P/surface area (2 sides) (μg/cm^2)

$= 2.66$ μg/{(1.1x1.1)/2 cm^2}

$= 1.10$ μg/cm^2

VITAE

Miss Sudarat Pookboonmee was born on August 29, 1981 in Bangkok, Thailand. She received a bachelor degree of science from Department of Chemistry, Faculty of Science, Kasetsart University, Bangkean, Bangkok, Thailand in 2004. In the same year she was admitted to a Master's Degree in Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University and completed program in 2007. Her address is Moo 5 Seekun, Donmuang, Bangkok 10210.