

CHAPTER III

EXPERIMENTAL

3.1 Materials

All reagents and materials are analytical grade

1. Propen-1-ol : Merck
2. Ammonium chloride : Merck
3. 2, 2'-Bipyridyl : Fluka
4. 2-Bromoisobutyryl bromide : Fluka
5. *tert*-Butyl methacrylate : Aldrich
6. Copper (I) bromide : Fluka
7. Copper (II) bromide : Fluka
8. Decen-1-ol : Aldrich
9. Dichloromethane : Merck
10. Diethyl ether : Carlo
11. Dimethoxyethane : Fluka
12. Dimethylethoxysilane : Gelest
13. Ethanol : Merck
14. Ethyl acetate : Merck
15. Ethyldiisopropylamine : Fluka

16. Hexadecane : Aldrich
17. Hexane : Merck
18. Hexen-1-ol : Aldrich
19. Hydrogen hexachloroplatinate (IV) hexahydrate : Aldrich
20. Hydrogen peroxide : Univar
21. Isopropyl alcohol : Merck
22. Magnesium sulfate anhydrous : Unilab
23. 2-Methacryloyloxyethyl phosphorylcholine : NOFcorporation, Japan
24. Methanol : Merck
25. *N, N, N', N'', N'''*-pentamethyldiethylenetriamine : Aldrich
26. Phosphate buffer saline (PBS) : Aldrich
27. 1-Propanol : Univar
28. Silica gel 60 (0.063-0.200 mm) : Merck
29. Silicon wafer (Single-sided) : Siltron Inc. Korea
30. Silicon wafer (Double-sided) : Siltron Inc. Korea
31. Sodium dodecyl sulfate : Fluka
32. Sodium sulfate anhydrous : Fluka
33. Sulfuric acid : Merck
34. Tetrahydrofuran : Carlo
35. Tris(trimethylsiloxy) chlorosilane : Gelest

36. Toluene : Carlo
37. Triethylamine : Carlo
38. Toluene anhydrous 99 % : Aldrich
39. Ultrapure distilled water : Mill-Q Lab system

3.2 Equipment

3.2.1 Ellipsometry

The ellipsometry was studied by using L115C WAFER™ ELLIPSOMETER. The thickness was determined in air with a 70° of incidence angle at 632.8 nm. The thickness of the adsorbed film was calculated by using the software “Dafibm” Rudolph Research, Double Absorbing Films Calculations. The calculation was based on a refractive index $N_{\text{initiator}} = 1.443$, $N_{\text{MPC}} = 1.488$, $N_{t\text{-BMA}} = 1.460$, $N_{\text{hydroxyl}} = 1.462$, $N_{\text{tris(TMS)}} = 1.386$ and a silicon substrate refractive index $N_{\text{substrate}} = 3.858$. At least five different locations on each sample were measured and the average thickness was calculated.

3.2.2 X-ray Photoelectron Spectroscopy (XPS)

X-ray photoelectron spectra were collected using ESCA-200, SCIENTA, Uppsala, Sweden. In this study, the take-off angle at 10° and 90° were chosen and the approximate of depth profile is ~10 and ~40 Å, respectively.

3.2.3 Nuclear Magnetic Resonance Spectroscopy (NMR)

The ^1H NMR spectra was recorded in CDCl_3 using Varian, model Mercury-400 nuclear magnetic resonance spectrometer operating at 400 MHz. Chemical shifts (δ) are reported in part per million (ppm) relative to tetramethylsilane (TMS) or using the residual protonated solvent signal as a reference.

3.2.4 Contact Angle Measurements

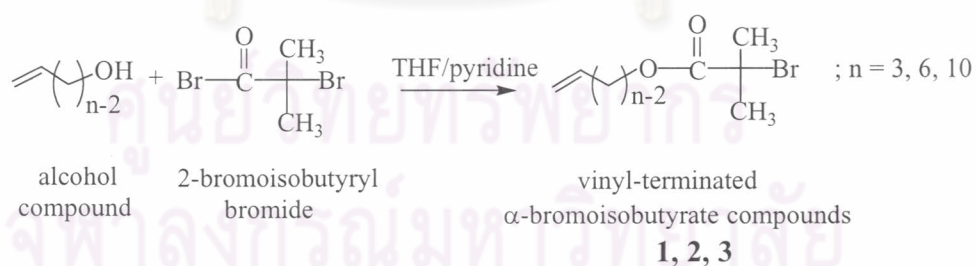
Contact angle goniometer was used for the determination of water contact angles. A droplet of probe liquid (Milli-Q water or hexadecane) is placed on the tested surface by bringing the surface into contact with a droplet suspended from a needle of the syringe. The measurements were carried out in air at the room temperature. Dynamic advancing and receding angles were recorded while water was added to and withdrawn from the drop, respectively. The reported angle is an average of 5 measurements on different area of each sample.

3.2.5 Atomic Force Microscopy (AFM)

AFM images were recorded with Atomic Force Microscope model SPI-3800, Seiko I, Tokyo, Japan. Measurements were performed in air using tapping mode. Silicon nitride tip with a resonance frequency of 13 kHz and a spring constant 0.02-0.1 N/m were used.

3.3 Synthesis of α -Bromoester Derivatives as Initiators

3.3.1 Synthesis of Vinyl-terminated α -Bromoisobutyrate Compounds



To a solution of 25 mmol of propen-1-ol (1.70 mL), hexen-1-ol (4.44 mL) or decen-1-ol (4.46 mL) in 25 mL of tetrahydrofuran, pyridine (2.1 mL, 26.5 mmol) was added, followed by a dropwise addition of 2-bromoisobutyryl bromide (3.10 mL, 25 mmol). The mixture was stirred at room temperature overnight, diluted with hexane and then washed once with 2N HCl and twice with deionized water. The organic phase was dried over sodium sulfate and filtered. After the solvent was

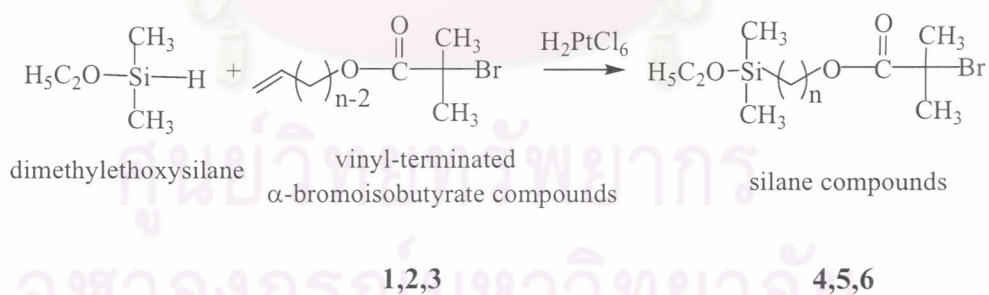
removed from the filtrate under reduced pressure, the colorless oily residue was purified by filtering through a silica gel column chromatography to give the product **1**, **2**, and **3** in 90, 85, and 85 % yield, respectively.

¹H NMR (CDCl₃) of 1 (n = 3): δ 1.98 (6H, C(CH₃)₂, s), 4.71 (2H, OCH₂, d, *J* = 5.46 Hz), 5.30-5.44 (2H, =CH₂, complex m), 5.93-6.0 (1H, =CH, complex m).

¹H NMR (CDCl₃) of 2 (n = 6): δ 1.90 (6H, C(CH₃)₂, s), 4.14 (2H, CH₂COO, d, *J* = 6.45 Hz), 2.09 (2H, C=CH₂CH₂, d, *J* = 7.04 Hz), 1.47 – 1.66 (4H, CH₂CH₂, d, *J* = 6.45 Hz), 4.96-5.04 (2H, =CH₂, complex m), 5.69-5.86 (1H, =CH, complex m).

¹H NMR (CDCl₃) of 3 (n = 10): δ 1.88 (6H, C(CH₃)₂, s), 4.14 (2H, CH₂COO, d, *J* = 6.44 Hz), 1.20-1.41 (12H, (CH₂)₆, d, *J* = 5.86 Hz), 4.87-4.99 (2H, =CH₂, complex m), 2.00 (2H, C=CH₂CH₂, complex m), 5.71-5.81 (1H, =CH, complex m).

3.3.2 Synthesis of Silane Compounds by Hydrosilylation of Vinyl-terminated α-Bromoisobutyrate Compounds



1 (87.52 mg, 4.23 mmol), **2** (105.28 mg, 4.23 mmol) or **3** (128.97 mg, 4.23 mmol) and dimethylethoxysilane (0.17 mL, 42.6 mmol) were mixed in a dry flask, followed by an addition of 0.2 mL of 1:1 ethanol/dimethoxyethane solution of chloroplatinic acid, H₂PtCl₆ (1.1 mg, 0.002 mmol). The reaction mixture was stirred at room temperature under nitrogen atmosphere in the dark for 14 h. Dry toluene (3 mL) was then added and the excess dimethylethoxysilane was removed under reduced pressure. Dry dichloromethane was added and then removed under reduced

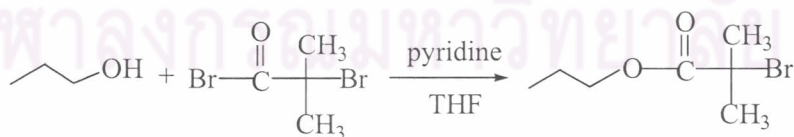
pressure. The crude product was passed through a short column of dry sodium sulfate, the column was washed with dry dichloromethane and the dichloromethane was removed under reduced pressure to give the desired product as yellow viscous liquid **4**, **5**, and **6** in 93, 90, and 90 % yield, respectively.

$^1\text{H NMR}$ (CDCl_3) of **4** ($n = 3$): δ 0.04 (6H, $\text{Si}(\text{CH}_3)_2$, s), 0.93 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$, t, $J = 7.04$ Hz), 1.24 (3H, $\text{SiOCH}_2\text{CH}_3$, t, $J = 7.04$ Hz), 1.66 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$, complex m), 1.88 (6H, $\text{C}(\text{CH}_3)_2$, s), 3.60 (2H, $\text{SiOCH}_2\text{CH}_3$, q, $J = 6.45$ Hz), 4.06 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$, t, $J = 6.45$ Hz).

$^1\text{H NMR}$ (CDCl_3) of **5** ($n = 6$): δ 0.06 (3H, CH_3SiCH_3 , s), 0.9 (3H, CH_3SiCH_3 , s), 1.15 (3H, $\text{SiOCH}_2\text{CH}_3$, t, $J = 7.04$ Hz), 1.20 – 1.33 (8H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, s), 1.6 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, complex m), 1.9 (6H, $\text{C}(\text{CH}_3)_2$, s), 3.63 (2H, $\text{SiOCH}_2\text{CH}_3$, q, $J = 6.45$ Hz), 4.04 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, t, $J = 7.04$ Hz).

$^1\text{H NMR}$ (CDCl_3) of **6** ($n = 10$): δ 0.05 (6H, $\text{Si}(\text{CH}_3)_2$, s), 1.22 (3H, $\text{SiOCH}_2\text{CH}_3$, t, $J = 7.03$ Hz), 1.3 (16H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_8$, s), 1.64 (2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_8$, q, $J = 7.03$ Hz), 1.89 (6H, $\text{C}(\text{CH}_3)_2$, s), 3.69 (2H, $\text{SiOCH}_2\text{CH}_3$, q, $J = 7.03$ Hz), 4.13 (2H, $\text{OCH}_2\text{CH}_2(\text{CH}_2)_8$, t, $J = 7.03$ Hz).

3.3.3 Synthesis of Prop-2-bromo-2-methylpropionate as a “Sacrificial” Initiator



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To a solution of 25 mmol of propanol in 25 mL of tetrahydrofuran, pyridine (3.1 mL, 26.5 mmol) was added, followed by a dropwise addition of 2-bromoisobutyryl bromide (3.10 mL, 25 mmol). The mixture was stirred at room temperature overnight and then diluted with hexane and washed once with 2N HCl

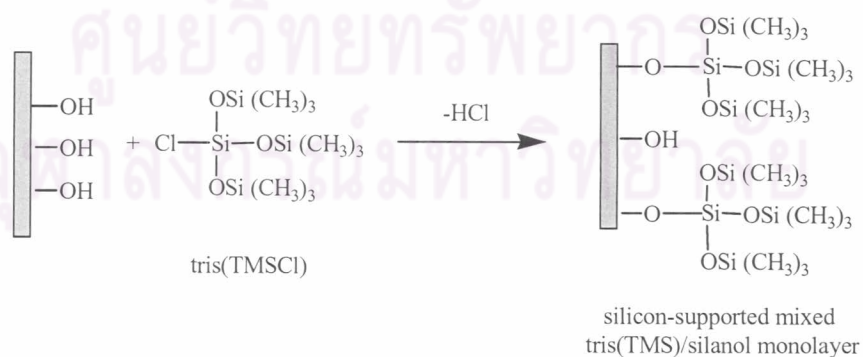
and twice with deionized water. The organic phase was dried over sodium sulfate and filtered. The solvent was removed from the filtrate under reduced pressure, and the colorless oily residue was purified by filtering through a silica gel column chromatography to give the desired product in 90% yield.

$^1\text{H NMR}$ (CDCl_3) of **7** : δ 1.0 (3H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, t, $J = 7.02$ Hz), 1.72 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, complex m), 1.95 (6H, $\text{C}(\text{CH}_3)_2$, s), 4.15 (2H, $\text{OCH}_2\text{CH}_2\text{CH}_3$, t, $J = 6.24$ Hz).

3.4 Pretreatment of Silicon Substrates

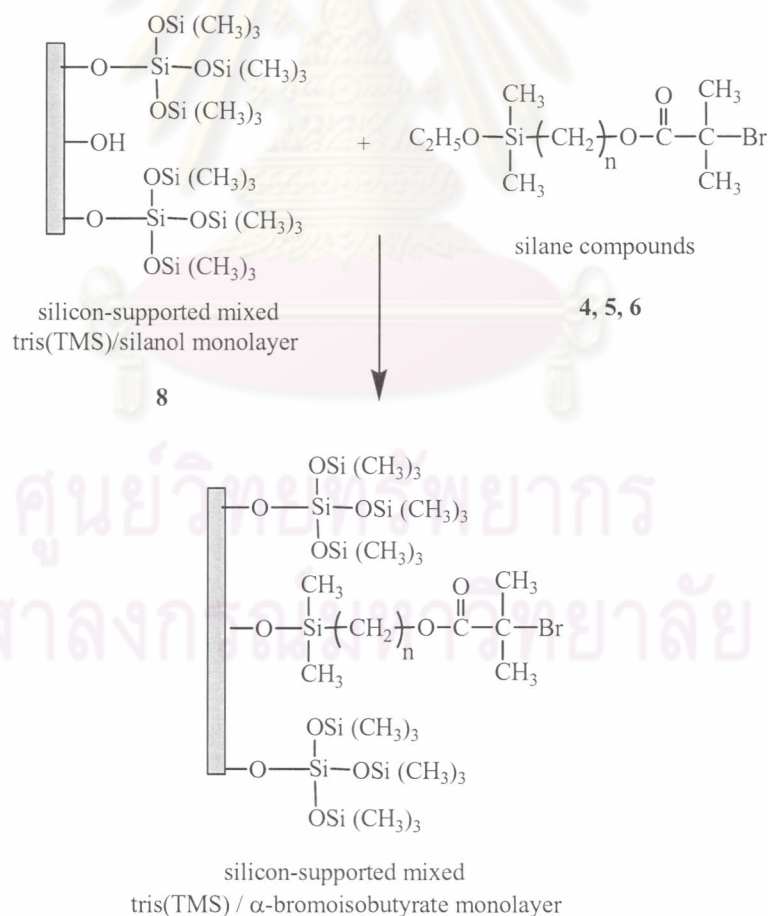
Silicon wafers were cut into $1.5 \times 1.5 \text{ cm}^2$ substrates. The substrates held in a slotted hollow glass cylinder (custom designed holder) were put in a freshly prepared mixture of 7 parts of concentrated sulfuric acid and 3 parts of 30% hydrogen peroxide. Substrates were submerged in the solution at room temperature for 2 h, rinsed with five to seven aliquots of deionized water and placed in a clean oven at 120°C for 2 h. Silanization reaction was carried out immediately after treating the substrates in this fashion.

3.5 Preparation of Silicon -supported Mixed Tris(TMS)/silanol Monolayer



Cleaned and dried silicon substrates held in a slotted hollow glass cylinder were covered with 10 mL of anhydrous toluene containing ethyldiisopropylamine (0.17 mL, 1 mmol) in a Schlenk flask. Tris(trimethylsiloxy)chlorosilane (tris(TMSPCl)) (0.35 mL, 1 mmol), was added by a syringe. Reactions were carried out at 60 – 70 °C for a predetermined period of time (1, 2, 3 and 4 days) under nitrogen atmosphere. The substrates were rinsed with 1 x 10 mL of toluene, 2 x 10 mL of 2-propanol, 2 x 10 mL of ethanol, 1 x 10 mL of ethanol-water (1:1), 1 x 10 mL of water and 1 x 10 mL of ethanol and then were dried in an oven at 120 °C for 10 min.

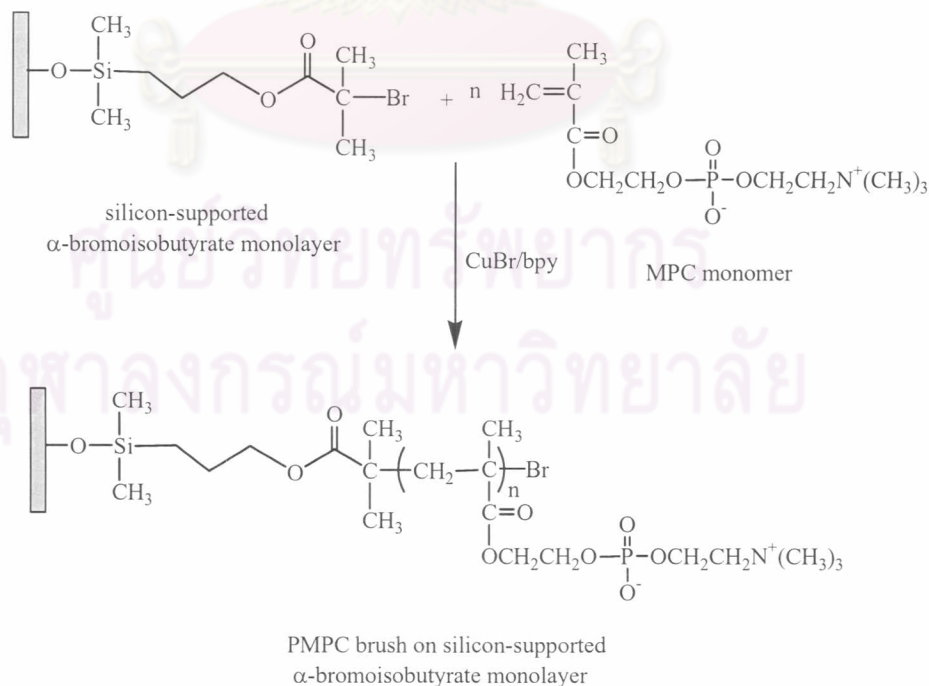
3.6 Preparation of Silicon-supported α -Bromoisobutyrate Monolayer and Silicon-supported Mixed Tris(TMS)/ α -Bromoisobutyrate Monolayer



Cleaned and dried silicon substrates or silicon-supported mixed tris(TMS)/silanol monolayer held in a slotted hollow glass cylinder were covered with 10 mL of anhydrous toluene containing ethyldiisopropylamine (0.17 mL, 1 mmol) in a Schlenk flask. 3-(Dimethylethoxysilyl)alkyl-2-bromoisobutyrate (**4**, **5**, or **6**, 0.15 mmol) was added by a syringe. Reactions were carried out under nitrogen atmosphere at ambient temperature for varying reaction time (1 – 4 days). The substrates were rinsed with 1 x 10 mL of toluene, 2 x 10 mL of 2-propanol, 2 x 10 mL of ethanol, 1 x 10 mL of ethanol-water (1:1), 1 x 10 mL of water and 1 x 10 mL of ethanol and dried under vacuum.

3.7 Preparation of Polymer Brushes

3.7.1 Surface-initiated Polymerization of 2-(methacryloyloxyethyl phosphorylcholine) (MPC)

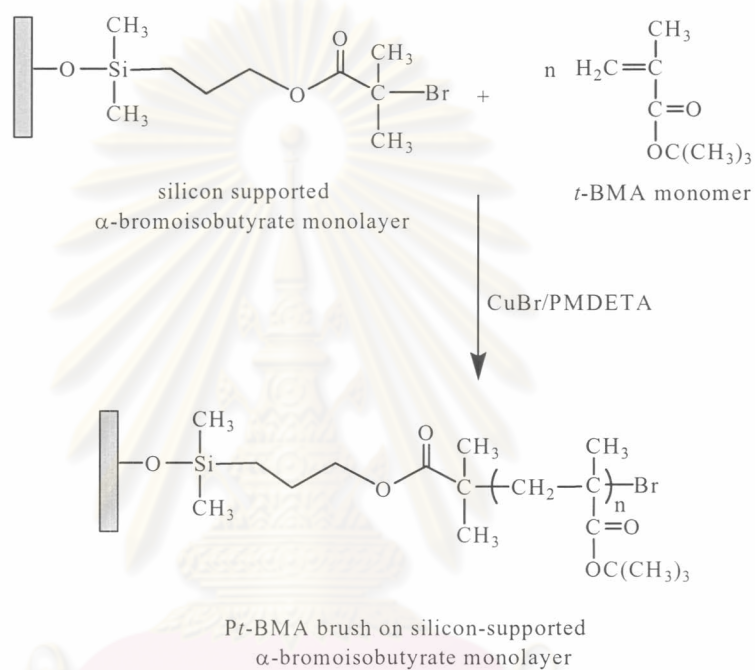


mixed tris(TMS)/ α -bromoisobutyrate monolayer held in a slotted hollow glass cylinder was then submerged into the flask. In the case of mixed solvent, MPC (3.6 g, 0.012 mol) was dissolved separately in 12 mL of methanol and purged with nitrogen for 1 h. In the case of pure methanol, 15 mL of methanol was used for solubilizing MPC. The MPC solution was added into the flask and polymerization was carried out at room temperature while stirring under nitrogen atmosphere. The silicon substrates were then removed from the polymerization mixture after the desired reaction time, rinsed with copious amount of methanol and water, respectively before soxhlet-extracted by methanol for 24h and dried under vacuum. PMPC formed in the solution from the “added” initiator was precipitated in cold THF. The viscous PMPC was re-dissolved in deionized water. The PMPC solution was passed through a silica column to remove copper catalyst before subject to dialysis and freeze-dried.

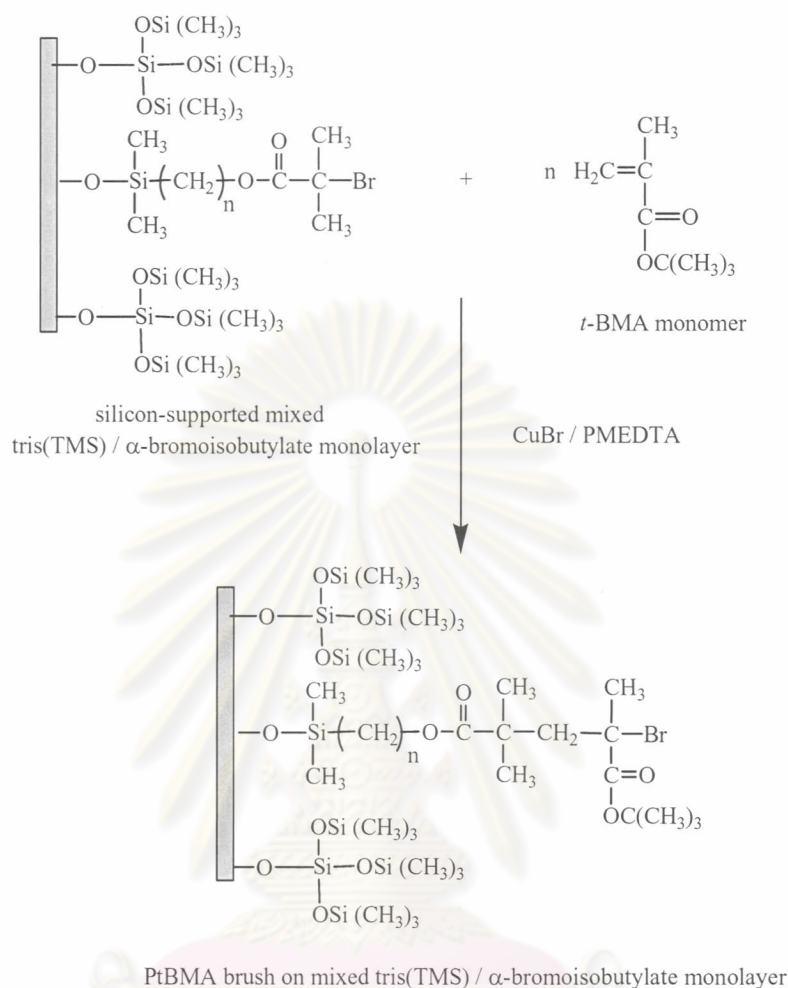
For the polymerization carried out in the presence of copper (I) bromide as an deactivator, the “sacrificial” initiator (7) was not added. The following content of reagents were used: copper (I) bromide (29 mg, 0.20 mmol), copper (II) bromide (4.4 mg, 0.02 mmol or 22 mg, 0.10 mmol), 2,2'-bipyridyl (63 mg, 0.40 mmol) and MPC (3.6 g, 0.012 mol). And copper (I) bromide was added simultaneously with copper (II) bromide.

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3.7.2 Surface-initiated Polymerization of *tert*-Butyl Methacrylate (*t*-BMA)



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Anhydrous toluene was used as a solvent for polymerization. It was distilled, degassed by two freeze-pump-thaw cycles and purged with nitrogen gas to eliminate oxygen before use. Copper (I) bromide (29 mg, 0.20 mmol) and PMEDTA (41.8 μL , 0.20 mmol) were dissolved in a Schlenk flask containing 15 mL anhydrous toluene. The solution was stirred under nitrogen atmosphere at 0°C. Then, propyl-2-bromoisobutyrate (7) (10 μL , 0.060 mmol) was added as a “sacrificial” initiator. After stirring for 30 min under nitrogen atmosphere, silicon-supported α -bromoisobutyrate monolayer or silicon-supported mixed tris(TMS)/ α -bromoisobutyrate monolayer held in a slotted hollow glass cylinder was then submerged into the flask. *t*-BMA (2.2 mL, 0.012 mol) was dissolved separately in 15

mL anhydrous toluene and purged with nitrogen for 1 h. The *t*-BMA solution was added into the flask and polymerization was carried out at 90 – 100 °C while stirring under nitrogen atmosphere. The silicon substrates were then removed from the polymerization mixture after the desired reaction time, rinsed with copious amount of toluene, before soxhlet-extracted by toluene for 24h and dried under vacuum. The solution containing *Pt*-BMA formed from the “added” initiator was past through a silica column to remove copper catalyst. Solid *Pt*-BMA was obtained after toluene was removed under reduced pressure.

For the polymerization carried out in the presence of copper (II) bromide as an deactivator, the “sacrificial” initiator was not added. The following content of reagents were used: copper (I) bromide (29 mg, 0.20 mmol), copper (II) bromide (4.4 mg, 0.02 mmol or 22 mg, 0.10 mmol), and bpy (63 mg, 0.40 mmol). Copper (I) bromide was added simultaneously with copper (II) bromide.



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