CHAPTER III

EXPERIMENTAL

3.1 Materials

Perfluoroalkylethyl methacrylate [$F(CF_2)_6CH_2CH_2COOCCH_3=CH_2$] (Aldrich, AR grade) and methyl methacrylate [$CH_3COOCCH_3=CH_2$] (Acros, AR grade) were used as monomers for copolymerization of PFMA-co-PMMA copolymer .Toluene [$C_6H_5CH_3$] (Labscan, AR grade) was use as solvent. Ethyl-2-bromoisobutyrate [$(CH_3)_2CBrCOOC_2H_5$] (AR Grade, Aldrich) was used as initiator. Copper(I)bromide [Cu(I)Br] (Aldrich, AR grade) and 4-amino benzoic acid [$C_7H_7NO_2$] (AR grade, Fluka) were used as catalyst and co-catalyst respectively. Sodium bromide [NaBr] (AR Grade,Unilab), ethanol[C_2H_5OH],(AR Grade, Labscan) ethyl acetate[$CH_3COOC_2H_5$] (AR Grade, Labscan) diethyl ether[$(C_2H_5)_2O$] (AR Grade, Labscan) and pentane[C_5H_{12}] (AR Grade, Univar) were use for copper(I) bromide purification.

Pyridene-2-carboxaldehyde (Aldrich, AR grade) and n- pentylamine (Aldrich, AR grade) were used as starting materials for the synthesis of N-^{n}pentyl-2-pyridinalmethanimine which was used as ligand.

Nitrogen gas (N_2 99% purity, TIG) was used as inert atmosphere for copolymerization of PFMA-co-PMMA.

Distilled water, purchased from the Thai Pharmaceutical Organization, Ethylene glylcol [$OHCH_2CH_2OH$] (JT Baker, AR Grade) and diiodomethane [CH_2I_2] (Acros, AR Grade) were used for the contact angle and the surface tension measurements.

1mm thick polymethyl methacrylate sheet (Towapex, commercial grade) was use as substrate for thin film coating.

3.2 Methodology

3.2.1 Statistical Copolymerization

3.2.1.1 Purification

MMA Monomer and solvents were passed down into a basic alumina column immediately prior to use (Handdleton, 1999). FMA momomer was distilled under vacuum at 200 °C (Park, 1997). Cu(I)Br were dissolved in boiling saturated aqueous NaBr over 30 min. Purred CuBr was obtained by cooling and diluting solution with water, followed by filtering and washing sequentially with H_2O, EtOH, EtOAc and Et_2O, pentane and then drying in a vacuum oven for 24 hour (Perrin, 1988). Other materials were used as received.

3.2.1.2 Synthesis of Ligand

An access of n- pentylamine (29.0 ml, 0.25 mol) was added dropwise to a stirred solution of pyridine-2-carboxaldehyde (20.0 ml, 0.21 mol) in diethyl ether, 20 ml) cooled in ice bath. After a complete addition of the amine, the reaction was continued for 30 min at ambient temperature before anhydrous magnesium sulphate (5g) was added and the slurry was stirred for a period of more 2 h. The solution was filtered, the solvent was removed, and the product was purified by distillation under 10 Torr, 80°C to give golden yellow oil (Haddleton, 1999).

3.2.1.3 Polymerization Procedure

The polymerization procedure was developed by following Haddlenton's method (Haddleton, 1999). [M]/[I]/[Cu]/[L]=100/1/1/2. Cu(I)Br(0.67 g,4.68×10^{-4} moles), benzoic acid (2.34×10^{-4} mole)and a magnetic stirrer were placed in a clean dry three-necked round bottom flask which was connected with nitrogen gas line and condenser(sealed at the top). The flask was flushed with nitrogen gas five times. The solution containing Toluene (5 ml.), N-^{n}pentyl-2-pyridinalmethanimine (0.173ml, 9.36×10^{-4} moles), Ethly-2-bromoisobutyrate (0.069ml, 4.68×10^{-4} moles) and monomer(4.68×10^{-4} moles) were deoxygenated by nitrogen purging for 15 min before adding into the reaction flask. The reaction flask was then placed in a preheated oil bath at 90 °C. (t=0). After 300 min, the reaction was stopped by shocking in iced bath for at least 30 min. Polymer solution was passed down into a basic alumina column and precipitated into n-pentane.

To investigate the effect of monomer mole ratios on properties, the mole ratios of FMA to MMA studied were 0:100, 0.05:99.95, 0.1:0.99.9, 0.2:99.8, 0.5:99.5, 0.7:99.3, 1:99, 10:90 and 20:80.

3.2.2 Testing and Characterization

3.2.2.1 Fourier-Transform Infrared Spectrometer (FT-IR)

FT-IR spectrometer (Bruker, FRA 106/S) was used to determine and compare the spectra of those polymers in the absorption mode with 32 scans at a resolution of 4 cm^{-1}. Samples were grounded with a mortar, mixed with KBr and molded into pellets under the pressure of 8 tons. The observed spectra were in the range of 400-4000 nm.

3.2.2.2 Mass Spectroscopy (MS)

Mass Spectroscopy (Fison, 7070E) was used to determine the structure of ligand, N-^{n}pentyl-2-pyridene-almethanimine, MS with VG data system using the positive Fast Atomic Bombardment (FAB^+-MS) mode and glycerol as matrix, CsI was used as reference and cesium gun was used as initiator.

3.2.2.3 Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (Oxford, 6111) was used to determine molar fraction of copolymer. A piece of sample was molded into pellet and placed on the holder with a conductive carbon adhesive tape. The percentages of each atom were obtained by using an acceleration voltage of 25.0 kV with the live time at 100 sec. The copper was use for calibration.

3.2.2.4 ^{1}H-NMR Spectrometer

1H-NMR spectrometer (Bruker, Advance DPX 400) operated at 300 MHz was used to determine molar fractions of copolymer. The polymer solutions were prepared by dissolving ~ 50 mg of polymer in 3 ml of deuterated chloroform ($CDCl_3$).

3.2.2.5 Gel Permeation Chromatography

The weight-average molecular weight, MW and polydispersity index, PI of copolymer were determined by gel permeation chromatography (Waters 150-C plus) with standard polystyrene calibrations. The column used was PLgel 10 μm mixed B 2 columns. Refractive index detector used as detector. THF was used as an eluent and the flow rate used was 1.0 ml/min.

3.2.2.6 Film Preparation

The spin coater (Cookson, P6700Seires) was use to prepare thin film coated specimen for contact angle measurements and friction testing. The polymer solution at concentration 5% by weight in toluene was dropped onto the 1mm thick PMMA sheet substrate which was cleaned in ultrasonic bath before used. The coated PMMA sheets were dried in a vacuum oven for 3 days at ambient temperature before testing.

3.2.2.7 Contact Angles and Surface Tension Measurement

Distilled water, diiodomethane, and ethylene glycol were used for contact angle and surface tension measurements. The sample was clamped to a flat surface and water (20 μl) was dispensed from a syringe which was suspended from above. The surface was raised and so that the needle was remained in the drop. The drop was advanced by dispensing a further 10 μl of water. A snap shot profile of the advanced drop was immediately captured to PC using a digital camera. The angle was then receded by withdrawing 10 μl. of water from the drop and another snapshot was captured. This process were repeated five times, the profiles were analyzed using Adobe Photoshop and the series of advancing and receding angles measured on the both sides of the drop were averaged. Diiodomethane and ethylene glycol were also following those steps to get various contact angles, which are later used for calculation, the surface tension values. The details of this calculation are in appendix F

3.2.2.8 Friction Testing

The Davenport friction testing apparatus, by Lloyd Instruments, was used to determine the static and kinetic friction coefficient. The sample was hold on the test bed by mean of a pressure sensitive adhesive tape. 1mm thick PMMA sheet, which was used as the reference, was cut and fixed to the underside for the sled. The total weight of the sled and the sled was 200 ± 5 g. The sled was drawn by a mechanical driver for 13 cm in distance and the speed was fixed at 150 ± 30 mm/min. The force required for starting movement of the sled or the static friction force was recorded. The force required for maintaining steady state movement or the sled dynamic friction force was continuously measured by the load cell as directly indicated by a force meter. The static and dynamic co-efficients of friction were calculated following Eq. (3) and Eq. (4) respectively:

$$\mu_s = A/W \qquad (3)$$

where μ_s is static co-efficient of friction, A is the starting force in grams and W is weights of the sled in grams;

$$\mu_k = B/W \qquad (4)$$

where μ_k is kinetic co-efficient of friction, B is steady state force in grams (average) and W is weights of the sled in grams.

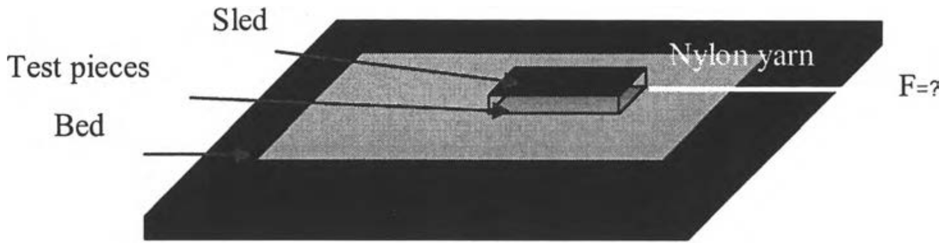

Figure 3.1 Schematic illustration of friction test by using Davenport Friction Testing Apparatus.

The dynamic friction coefficient measurements was also investigated by using Multi –axis tribometer, model TE-79, from Plint Tribology Ltd. Steel ball (diameter 12.7 mm), made of ball bearing steel was drawn over the surface with the normal load at 800 g. A constant rotational speed of 10 rpm and the rotational radius of 20 mm were used in all experiments. All experiments were performed at a controlled room temperature (22-25 °C). During each experiment, friction force was continuously recorded. In the test series two, both single and multipass experiments were performed.

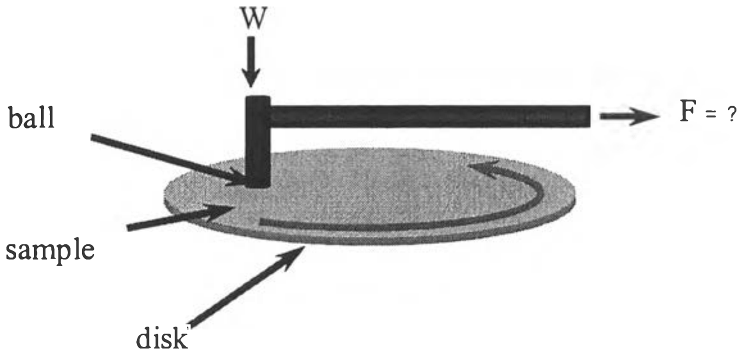

Figure 3.2 Schematic illustration of friction test by using TE 79 Multi – axis Tribometer.

3.2.2.9 Surface Characterization

The scratched samples without further modification from 3.3.2.8 were thoroughly investigated by optical microscopy (Leica, DMRXP). The measurement was performed in the transmitted light mode. The magnification was 6.4: 4 magnification for the objective lens and 1.6 magnification for eyes lens.