SUPPORTING INFORMATION FOR:

Strong and Tuneable Wet Adhesion with Rationally Designed Layer-by-Layer Assembled Triblock Copolymer Films

Andrea Träger, Samuel A. Pendergraph, Torbjörn Pettersson, Tobias Halthur, Tommy Nylander, Anna Carlmark and Lars Wågberg*

* corresponding author, wagberg@kth.se
Polymer synthesis and characterisation

Figure 1 shows a reaction scheme of the synthesised polymers.

Chemicals

Triethylamine (TEA), Merck and Pentamethyl diethylene triamine (PMDETA), Methyl iodine (MeI), Hexamethyl triethylene tetraamine (HMTETA), Bromoisobuturyl bromide (BiB) and Trifluoroacetic acid (TFA) as well as reagent grade solvents – Methanol (MeOH), Tetrahydrofuran (THF), Ethyl acetate (EtOAc), N-Methylmorpholine N-oxide (NMNO), Dichloromethane (DCM), Dimethyl Sulphoxide (DMSO), and Toluene – from Sigma Aldrich were used as received. Copper(I)chloride (CuCl), and Copper(I)bromide (CuBr), Sigma Aldrich were purified as described in literature. Tert-butyl methacrylate (t-BMA), Dimethyl aminoethyl methacrylate (DMAEMA), n-butyl methacrylate (n-BMA), Sigma Aldrich and 2-ethyl hexyl methacrylate (EHMA), Alfa Aesar were destabilized before use by running through a column of neutral aluminum oxide. Poly(vinyl amine) (PVAm) with the tradename Lupamin 9095 Special, BASF, was dialyzed and freeze-dried before use. Analytical grade potassium poly(vinyl sulphate) (KPVS), Wako Chemicals was used as received. Poly(diallyldimethyl ammonium chloride) (PDADMAC), Sigma Aldrich was dialyzed and freeze dried prior to use.

Synthesis

**Difunctional Initiator:** 7.45 ml of TEA was added to a roundbottom flask equipped with magnetic stirrer along with 60 ml of THF and the flask placed in a water/ice bath. 6.61 ml (53 mmol) of BiB was added dropwise to this solution which was then left to stir for 10 minutes before 2 ml (19 mmol) of pentane diol diluted with 20 ml of THF was added dropwise. After 24 h the precipitate was filtered off, and the solvent evaporated. The remainder of the liquid phase was redissolved in 200 ml of EtOAc and extracted thrice with 30 ml of each of the following: deionized water, 2M NaOH(aq), deionized water , 2M HCl, deionized water. Lastly, the solution was dried with MgSO₄ before removal of the EtOAc by rotary evaporation followed by drying under reduced pressure over night, leaving the product as a yellow oil in 90% yield.

**Macroinitiator:** 54 mg (0.13 mmol) of difunctional initiator, 5 ml of toluene, 153 µl (0.56 mmol) of HMTETA and 15 ml (66.9 mmol) of EHMA were added to a roundbottom flask equipped with magnetic stirrer and placed in an ice bath. After 5 min of vacuum followed by 5 min of purging with Ar(g), 40 mg (0.28 mmol) of CuBr was added before two additional vacuum-argon cycles were performed. The roundbottom flask was then placed in an oil bath at 70 °C. The reaction was monitored by ¹H-NMR, and terminated at a conversion of 30 % by first cooling the reaction flask to 0 °C in an ice bath and then opening to the atmosphere. The reaction mixture was diluted with DCM and filtered through a short column of neutral alumina to remove the Cu before precipitation thrice in MeOH cooled by a dry ice/acetone bath, followed by drying under reduced pressure overnight. Synthesis of the n-BMA macroinitiator was performed analogously; the EHMA and n-BMA macroinitiators gave yields of 87% and 92%, respectively.

**Triblockcopolymers:** Chain extension of PEHMA macroinitiator with DMAEMA was performed according to the following. 950 mg (0.03 mmol) of PEHMA macroinitiator was dissolved in 1 ml of a 3/7 acetone/toluene volume-by-volume mixture along with 25 mg (0.11 mmol) HMTETA and 257 mg
(1.63 mmol) DMAEMA in a roundbottom flask. The mixture was degassed and 5.39 mg (0.05 mmol) CuCl added in the same manner as during the macroinitiator synthesis. The roundbottom flask was then placed in an oil bath at 50 °C, the reaction monitored by 1H-NMR, and terminated at 30% monomer conversion as described above. The polymer was isolated as described for the macroinitiator. 480 mg of PDMAEMA-PEHMA-PDMAEMA was dissolved in 25 ml THF in a roundbottom flask equipped with a magnetic stirrer. Then the flask was placed in an ice bath and 1 ml of Mel, separately diluted with 5 ml of THF, was added dropwise to the polymer solution. The reaction mixture was left at room temperature overnight, and the solvent and residual Mel were then evaporated under reduced pressure. Synthesis of QPDMAEMA-PBMA-QPDMAEMA was performed analogously.

The chain extension of PEHMA with t-BMA was performed similarly to the previously described ATRP syntheses; 950 mg (0.03 mmol) of PEHMA, 19 mg (0.05 mmol) PMDETA and 232 mg (1.63 mmol) t-BMA and 1 ml of toluene were mixed in a round bottom flask at 70 °C. Again, the corresponding PBMA based copolymer was synthesized analogously to PMAA-PEHMA-PMAA. Deprotection of the tBMA block was performed by dissolving the polymer in DCM and adding an excess of TFA. This mixture was allowed to stir in room temperature for 6 h before the solvent and TFA were evaporated under reduced pressure and the residue dialyzed against deionized water for two days. The yields for the PDMAEMA and Pt-BMA chain extensions from PEHMA were 63% and 65%, respectively and for the same outer blocks from PBMA 66% and 69%, respectively. Quaternisation and deprotection reactions were near quantitative.

The four triblock copolymers will be denoted PEHMA+ (for the QPDMAEMA-PEHMA-QPDMAEMA copolymer), PEHMA- (PMAA-PEHMA-PMAA), PBMA+ (QPDMMAEMA-PBMA-QPDMAEMA) and PBMA- (PMAA-PBMA-PMAA), respectively, throughout the text.

Characterisation

Differential Scanning Calorimetry (DSC) was performed with a Mettler Toledo, DSC 820 in N₂, the samples were first heated to 180 °C and cooled to -60 °C to erase the thermal history and subsequently heated to 180 °C again, at a heating rate of 10 °C/min. Size Exclusion Chromatography (SEC) was performed in a Verotech PL-GPC 50 Plus equipped with a PL-RI detector and two PLgel 5 mm MIXED-D columns, 300 x 7.5 mm (Varian). Samples were injected with a PLAS RT autosampler (Polymer Laboratories) with chloroform as the mobile phase at a flow rate of 1 ml/min at 30 °C and toluene as internal standard. The calibration was set using polystyrene standards with a narrow molecular weight distribution ranging from 160 000-371 000 g/mol. 1H-NMR spectra were recorded with a Bruker Avance 400 MHz with CDCl₃ as solvent.
Synthesis of middle block

Chain extensions

Figure 1 Reaction scheme for the synthesized triblock copolymers. “R” is either an n-butyl or 2-ethyl hexyl group. If not otherwise stated in the figure, the reaction step was performed at room temperature.
Preparation of cellulose model surfaces

The charge density of the fibres was modified to 350 µeq/g by carboxymethylation according to a previously described method. The dried pulp was dissolved in NMMO (50 % aq.) at 125 °C and a concentration of 20 mg/ml. Then, the mixture was diluted to four times its original volume by DMSO. This solution was then spin coated (Spin-coater KW-4A, Chemat Technology), for 15 s at 1500 rpm followed by 30 s at 3500 rpm onto a silicon wafer (p-type, MEMC Electronic Materials) or QCM crystal (AT-cut quartz crystals with silicon oxide surface. Q-sense) which had previously been placed in an air plasma cleaner (PDC 002, Harrick Scientific Corporation.) for 2 min ta high effect, then dipped in PVAm for 15 min, rinsed with MilliQ water and blown dry by N₂(g). Poly (vinyl amine) was used as anchoring layer between the substrate and cellulose film, to secure a sufficient wet adhesion between them.

Estimation of the length of an extended molecule of EHMA-

Typical values for the length and angle of carbon-carbon single bonds are presented in figure 2. Using trigonometry the distance between the two outer carbons in the figure is calculated to 2.5 Å. This corresponds to the length of the backbone of one repeat unit in the polymer chain. Then this value is multiplied with the DP of EHMA-, giving an estimated chain length of 51.5 nm = 50 nm.

![Figure 2 Typical bond angle and length of a C-C bond](image)

Additional results from characterisation of the neat polymers

Nuclear Magnetic Resonance spectra

Figure 2 through 7 show Nuclear Magnetic Resonance (NMR) spectra with assigned peaks for the homopolymers making up the middle blocks of the triblock copolymers, and the precursors to the final triblock copolymers (before quaternisation of the tertiary amine, or deprotection to remove tert-butyl group). Chemical structure of the polymer is shown on the corresponding figure.
Figure 3 $^1$H-NMR spectrum of PEHMA macroinitiator

Figure 4 $^1$H-NMR spectrum of PDMAEMA-PEHMA-PDMAEMA
Figure 5 $^1$H-NMR spectrum of PtBMA-PEHMA-PtBMA

Figure 6 $^1$H-NMR spectrum of PBMA macroinitiator
Figure 7 $^1$H-NMR spectrum of PDMAEMA-PBMA-PDMAEMA

Figure 8 $^1$H-NMR spectrum of PtBMA-PBMA-PtBMA
Size exclusion chromatography chromatograms
Figure 8 through 11 show chromatograms from size exclusion chromatography (SEC) for the precursors to the final triblock copolymers (the red curve on each graph) together with the corresponding homopolymer making up the middle block of said triblock copolymer (the black curve on each graph).

Figure 9 SEC chromatogram of PEHMA macroinitiator and precursor to PEHMA+
**Figure 10** SEC chromatogram of PEHMA macroinitiator and precursor to PEHMA-

**Figure 11** SEC chromatogram of PBMA macroinitiator and precursor to PBMA+
Figure 12 SEC chromatogram of PBMA macroinitiator and precursor to PBMA-
Additional results from characterisation of the micelle dispersions and their adsorption behaviour

Figure 12 shows the refractive index as a function of number of bilayers for the PEHMA system, measured by ellipsometry. Standard deviation of the average is show as error bars. Figure 13 shows refractive index as a function of number of bilayers for the PBMA system.

Figure 12 Refractive index of LbL films of the PEHMA system measured by ellipsometry

Figure 13 Refractive index of LbL films of the PBMA system measured by ellipsometry
Figure 14 shows an example of a representative cryo-TEM picture of a micelle dispersion. The darker, circular shapes on the picture are micelles. The sample was flash-frozen, so there was no directional order and the ice is amorphous. Since all structures seen have a circular shape and similar intensity they are uniform in 3D, *i.e.* spherical.

![Representative cryo-TEM image of the polymer micelles](image)

**Figure 14** Representative cryo-TEM image of the polymer micelles

Table 1 summarises the root mean square roughness of the LbL films, as an average over 2-3 AFM images, each 2x2 μm in size.

**Table 1** root mean square roughness of LbL films

<table>
<thead>
<tr>
<th>Polymers</th>
<th>n/o of bilayers</th>
<th>Average roughness Rq [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>neat mica</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>PEHMA+/PEHMA-</td>
<td>0.5</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.0</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.9</td>
</tr>
<tr>
<td>PBMA+/PBMA-</td>
<td>0.5</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>1.5</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.5</td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>2.5</td>
</tr>
</tbody>
</table>
Figures 15 through 18 show results from QCM measurements with silica as substrate.

**Figure 15** QCM graph of PEHMA+ (denoted "+") and PEHMA- (denoted "-") adsorbing to a silica surface

**Figure 16** QCM graph of PEHMA+ (denoted "+"") and PEHMA- (denoted "-"") adsorbing to a silica surface
Figure 17 QCM graph of PBMA+ and PBMA- adsorbing to a silica surface

Figure 18 QCM graph PEHMA+ (denoted "+") and PEHMA- (denoted "-" ) adsorbing to a silica surface, with 10 mM NaCl present in micelle dispersions and rinsing solution
Comparison of present results with literature

Table 1 shows a comparison of literature where adhesion has been measured by colloidal probe AFM in liquid state. If several conditions were evaluated in a paper, the highest value reported in the paper is the one reported here, even if those conditions were more beneficial than the ones used in the present study. When no normalised value was reported in the paper, the normalised value below was based on the radius of the probe stated in the paper.

Table 2 Comparison of the present result with literature where adhesion has been measured by force probe AFM in liquid state.

<table>
<thead>
<tr>
<th>System</th>
<th>Result</th>
</tr>
</thead>
</table>
| **Cellulose thin film and spherical cellulose probe coated** with monolayer of phenyl boronic acid functionalised polyvinylamine | Pull-off force\(^3\) \(\approx\) 15 nN  
Normalised pull-off force: \(\approx 1.5 \text{ mN/m}\) |
| **Three bilayers of poly (allylamine hydrochloride/hyaluronic acid adsorbed on a spherical silica probe and silica wafer, 10s surface delay** | Normalised pull-off force\(^6\): \(\approx 16 \text{ mN/m}\) |
| **Borosilicate glass sphere coated with a monolayer of polyethylene imine and silica wafer coated with 5 bilayers of polyethyleneimine and poly(sodium styrenesulphonate)** | Pull-off force\(^7\) \(\approx\) 85 nN  
Normalised pull-off force: \(\approx 17 \text{ mN/m}\) |
| **Self-assembled structures of mussel foot protein and CsgA proteins** | Normalised pull-off force\(^4\): \(\approx 130 \text{ mN/m}\) |
| **Present study, EHMA system with 5 mM salt present during adsorption** | Normalised pull-off force: \(\approx 150 \text{ mN/m}\) |