

# PH-RESPONSIVE “SMART SURFACE COATINGS”

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## ABSTRACT

A diblock copolymer poly(2-(dimethylamino)ethyl methacrylate)-*block*-poly(2-(diethylamino)ethyl methacrylate) (PDEAEMA-*b*-PDMAEMA) was prepared via reversible addition fragmentation chain transfer (RAFT) polymerization, using 2-cyanoisopropyl dithiobenzoate (CPDB) as the RAFT agent. Characterization of these polymers by <sup>1</sup>H NMR and size exclusion chromatography (SEC) indicated that the copolymers had a well controlled microstructure. The micellization behavior of this copolymer sample, in aqueous solution, was investigated by dynamic light scattering and AFM; a reversible unimer to micelle transition at pH~7.5 was seen with the micelles formed at higher pHs. After deposition of a monolayer of micelles at the solid-liquid interface, contact angle measurements as a function of pH showed that a pH-responsive surface-coating had been obtained.

**Keywords.** Block copolymers, micelles, reversible addition fragmentation chain transfer (RAFT), pH-responsive surface.

## 1 INTRODUCTION

Over the last few years, adsorption of polyelectrolyte micelles at the solid/liquid interface has gained in popularity due to their potential applications for drug delivery, for the preparation of nanosized materials and for the fabrication of smart surface coatings.

One route for the development of such a smart surface coating involves the use of stimulus-responsive amphiphilic diblock copolymers. An example of such a system is based on polymethacrylate derivatives, and in particular on dimethylaminoethyl methacrylate (DMAEMA) and diethylaminoethyl methacrylate (DEAEMA). Much work has been reported for diblock

copolymers of PDEAEMA-*b*-PDMAEMA synthesised by group transfer polymerization (GTP) [1,2], or atom transfer radical polymerization (ATRP) [3,4].

RAFT polymerization is a controlled/living polymerization that can produce well-defined homopolymers and block copolymers [5,6]. As DMAEMA has previously been successfully polymerized by CPDB mediated RAFT process [7], this method of polymerization was chosen to prepare such a PDEAEMA-*b*-PDMAEMA copolymer. The lack of data relating to RAFT copolymerization of DEAEMA and DMAEMA motivated us to investigate this system further.

Herein we provide detailed RAFT polymerization kinetics of PDEAEMA using the RAFT agent, 2-cyanoisopropyl dithiobenzoate (CPDB) that generally affords well-controlled polymethacrylate derivatives [6]. We also demonstrate the synthesis of diblock copolymers of PDEAEMA-*b*-PDMAEMA. Moreover, we present evidence that aqueous solutions of these block copolymers show reversible pH-responsive micelle formation. Here we investigate whether surface adsorbed films of these micelles also show reversible pH responsive characteristics.

## 2 EXPERIMENTAL SECTION

### 2.1 Materials.

All solvents, monomers and other reagents (Aldrich) were used as received unless otherwise stated. Azobisisobutyronitrile (AIBN) was purified by recrystallization from hot methanol prior to use. DEAEMA and DMAEMA were passed through a column of basic alumina to remove the inhibitor. CPDB was synthesized and purified as previously reported [6].

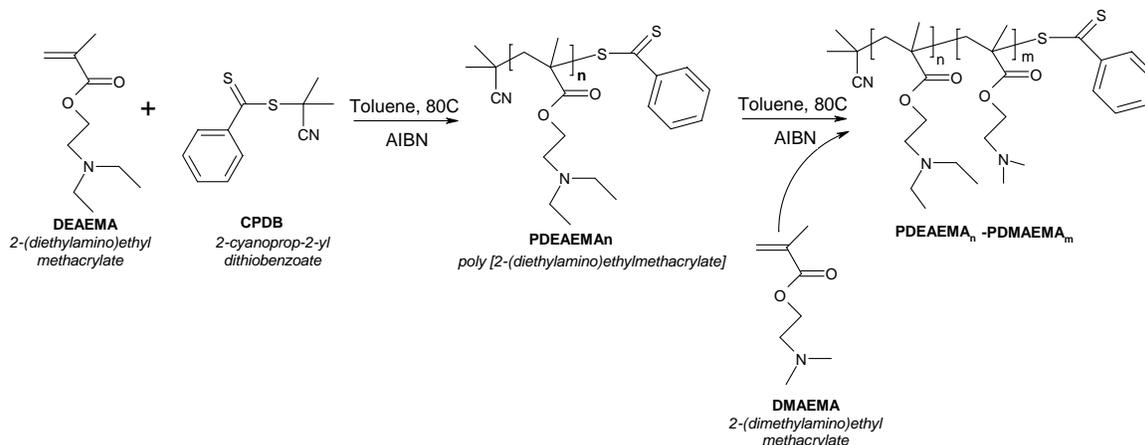


Figure 1 : Synthesis procedure of PDEAEMA-*b*-PDMAEMA by RAFT polymerization

## 2.2 Polymerization procedure.

### RAFT Polymerization of DEAEMA mediated by CPDB.

DEAEMA (2.78 g, 15.05 mmol), CPDB (0.113 g, 0.51 mmol), AIBN (34 mg, 0.207 mmol) and toluene (solvent, 0.73g, 25% in mass) were introduced in a Schlenk tube containing a magnetic stirrer. The mixture was separated in several samples. All of the samples were degassed by nitrogen bubbling and heated at 80°C in a thermostated oil bath under nitrogen atmosphere. After a given time of polymerization (Figure 2), the vial was immersed into ice to stop the polymerization. Conversion was determined by <sup>1</sup>H NMR spectroscopy at 400 MHz, integrating one vinylic proton (6.11 ppm) in comparison with triplet peak (at 4.2 ppm, from the monomer CH<sub>2</sub>) + large peak (at 4.1 ppm, from CH<sub>2</sub> polymer). Molar masses and polydispersity indices were determined by SEC using PMMA standard calibration and THF as eluent.

### Synthesis of Poly(2-(diethylamino)ethylmethacrylate)-block-poly(2-(dimethylamino)ethylmethacrylate) (PDEAEMA-*b*-PDMAEMA)

A similar procedure was used with PDEAEMA<sub>29</sub> as macroRAFT agent ( $M_{n,SEC} = 5990$  g/mol,  $M_{n,th,NMR} = 5605$  g/mol, PDI = 1.16). The following amounts were used DMAEMA (7.8 g, 49.6 mmol), MacroRAFT agent (2.78 g, 0.5 mmol), AIBN (32 mg, 0.2 mmol) and toluene (solvent, 2.8 g, 25% in mass). The copolymerization was conducted at 80°C in toluene (25% in mass), for 3 hours (conversion of DMAEMA of 95%). Copolymers were purified by precipitation in cold hexane and then were analysed using SEC in THF and NMR. ( $M_{n,SEC} = 16890$  g/mol,  $M_{n,th,NMR} = 20540$  g/mol, PDI = 1.34).

## 2.3 Polymer characterization.

<sup>1</sup>H NMR spectroscopy was carried out on a Bruker (400MHz) NMR instrument with CDCl<sub>3</sub> as a solvent and tetramethylsilane as a reference.

SEC. The molecular weight distributions were measured by SEC at the ambient temperature with a system equipped with a guard column and mixed C columns (Polymer Laboratories) with a differential refractive index detector. Tetrahydrofuran was used as eluent (flow rate 1 mL.min<sup>-1</sup>). Toluene was used as a flow rate marker.

Atomic Force Microscopy: A Nanoscope IV (Veeco, CA) atomic force microscope (AFM) was used for in-situ imaging of adsorbed PDEAEMA-PDMAEMA micellar layers at the solid-liquid interface. Cantilevers with an integral silicon nitride tip (NanoProbe, Veeco, CA) were used for all AFM experiments and were cleaned using UV irradiation prior to use. All solutions were passed through a syringe-mounted 0.2µm filter as they were injected into the AFM fluid cell. At the beginning of experiment, a 0.01M KNO<sub>3</sub> solution at pH 9 was injected into the fluid cell, enabling the mica to equilibrate to the experimental pH conditions. The images were collected using soft-contact technique.

Contact Angle Measurements. A CAM 200 (KSV instruments) was employed to measure static contact angles on glass slide. Glass slides were dipped 4 hours in a beaker containing a copolymer solution (500 ppm) at pH 9 (Borax solution). After drying these samples at room temperature (RT), glass slides were rinsed with Milli-Q® water (~5 mL) in order to remove the excess of copolymer. Then, they were dried again at RT, and static contact

angles have been measured by using a drop of Milli-Q® water or of a KNO<sub>3</sub> (0,01M) solution at a desired pH. The pH was adjusted with dilute KOH or HNO<sub>3</sub> solutions

## 2.4 Micellar Solution Preparation

Block copolymer sample (500 ppm) was directly dissolved in 0.01 M aqueous KNO<sub>3</sub> solutions at pH 4 by using small amount of diluted HNO<sub>3</sub> in order to enhance the solubility of the copolymer. After stirring overnight, the pH of the copolymer solution was adjusted to 9 immediately prior to use. This pH change results in micellization of the diblock copolymers without use of any organic solvents.

## 3 RESULTS AND DISCUSSION

PDEAEMA-PDMAEMA copolymer prepared by GTP and ATRP is already known to be a pH responsive block copolymer [1-4]. A block ratio of 30/90 should allow the formation of aggregates in solution and so, we decided to focus on the RAFT synthesis of PDEAEMA<sub>30</sub>-PDMAEMA<sub>90</sub> copolymer and its behavior in solution.

### 3.1 RAFT synthesis of DEAEMA homopolymer

Firstly, we studied the RAFT polymerization kinetics (Figure 2) for the synthesis of PDEAEMA with a targeted polymerization degree of 30. CPDB and AIBN were, respectively, used as RAFT agent and initiator in this study. Typically, the general condition of polymerization was at 80°C in toluene (25% in mass), using the following ratios: [DEAEMA]/[CPDB]/[AIBN]: 30/1/0.4. The conversion of DEAEMA was determined by NMR and the molar masses by SEC.

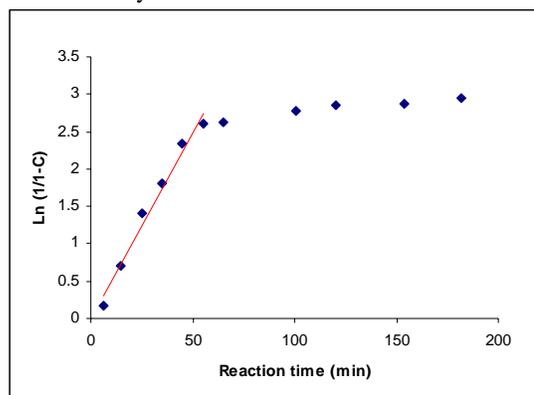


Figure 2: PDEAEMA polymerization kinetics performed at 80°C in toluene (25% in mass), [DEAEMA]/[CPDB]/[AIBN] : 30/1/0.4.

The experimental molar masses were compared to theoretical values calculated according to equation (1).

$$M_{n,th,NMR} = M_{CPDB} + M_{DEAEMA} \times \frac{[DEAEMA]_0 \times C_{DEAEMA}}{[CPDB]_0} \quad (1)$$

where  $M_{CPDB}$  and  $M_{DEAEMA}$  are the molar masses of CPDB and DEAEMA, respectively  $[CPDB]_0$  and  $[DEAEMA]_0$ , the initial concentration of CPDB and DEAEMA and  $C_{DEAEMA}$ , the fraction conversion. The contribution of the molar mass of the chains initiated by AIBN was neglected.

The number average molar mass is plotted against conversion in Figure 3. A linear relationship was found, thus demonstrating that the molecular weight could be predicted depending on conversion. Higher-than-theory molecular weights were obtained, as the SEC was

calibrated with PMMA standards rather than PDEAEMA. The low polydispersities obtained throughout the polymerization ( $PDI < 1.2$ ) shows that the polymerization is well controlled. Figure 2 and Figure 3 confirm the living character of the polymerization.

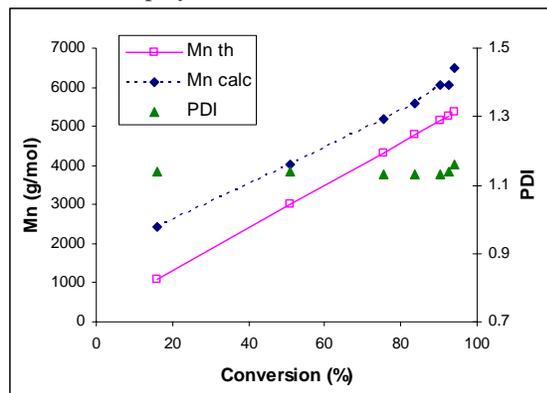


Figure 3: Evolution number average molar masses ( $M_n$ ) and polydispersity ( $PDI$ ) versus conversion obtained by SEC using PMMA standards and THF as eluent.

### 3.2 RAFT synthesis of PDEAEMA-*block*-PDMAEMA copolymer.

For the synthesis of the diblock PDEAEMA-*b*-DMAEMA copolymers, a RAFT synthesized PDEAEMA<sub>29</sub> (conversion 97%) was used as the macroRAFT agent. Chain extension experiments were carried out to get PDEAEMA-*b*-DMAEMA copolymers. This proves the living character of PDEAEMA chains obtained by CPDB-mediated RAFT polymerization.

The following ratios were used: [DMAEMA]/[macroRAFT agent]/[AIBN]: 100/1/0.4, at 80°C in toluene (25% in mass). Samples were withdraw after 3 hours (conversion of DMAEMA of 95%), and the obtained copolymers were analyzed by SEC in THF and NMR. The observed shift of the chromatogram confirm the successful extension of the polymeric chains (Figure 4). We observe a shoulder at high molar mass on the molecular weight distributions of the copolymer (low elution time), potentially due to bimolecular termination. Both the high molar mass shoulder and the low molar mass homopolymer broaden the molar mass distribution and reduce the living character and purity of the block copolymer. Indeed, a polydispersity index of 1.34 was obtained.

### 3.3 Behavior in solution

PDEAEMA-PDMAEMA copolymers are known to reversibly form micelles at some critical pH in aqueous solution: they are molecularly dissolved in acidic solution as a result of protonation of both the blocks. As the pH is increased both blocks are deprotonated and at the critical pH, they spontaneously form polymeric micelles with the more hydrophobic PDEAEMA chains located in the cores and the PDMAEMA chains forming the micelle coronas. In Figure 5, under acidic conditions, the block copolymers are observed to exist as unimers (Hydrodynamic diameter  $D_H \approx 8-9$  nm), while under basic conditions they self assemble into polymeric micelles ( $D_H \approx 27-28$  nm). The critical pH range for the PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> used in this study is 7.3- 7.8.

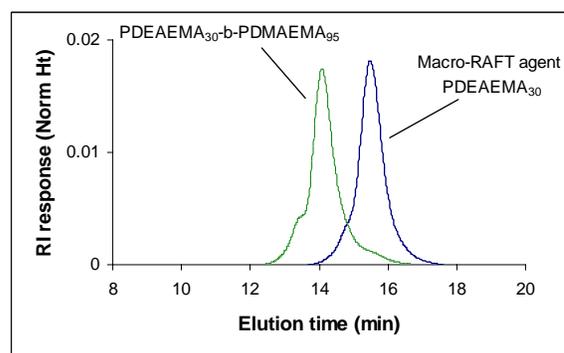


Figure 4 : SEC chromatogram of PDEAEMA<sub>30</sub> homopolymer used as macro RAFT agent and PDEAEMA<sub>30</sub>-*b*-DMAEMA<sub>95</sub> copolymer.

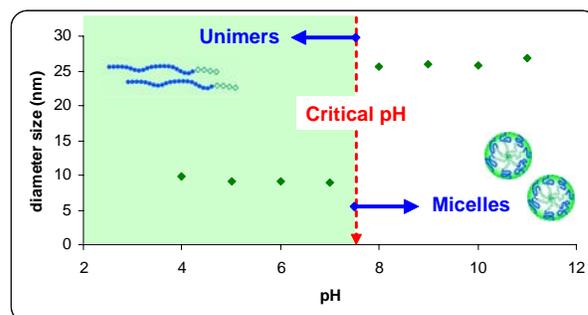


Figure 5 : Change in hydrodynamic diameter of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> as a function of pH.

### 3.4 Adsorbed layer morphology.

The adsorption of such diblock copolymer micelles has previously been described at the mica and silica/aqueous solution interfaces [4,8,9,10]. These cationic copolymer micelles adsorb strongly on both surfaces at pH 9 (on mica see Figure 6 A), and respond reversibly to changes in solution pH.

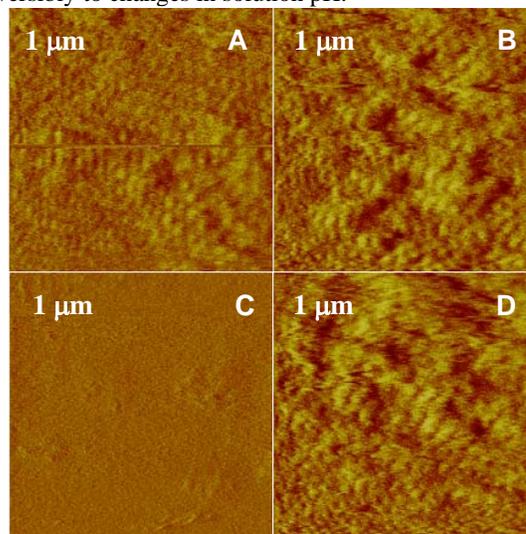


Figure 6 : In situ soft-contact AFM images of PDEAEMA-DMAEMA micelles adsorbed from a 500 ppm solution at pH = 9 on mica. A) 50 min after solution injection at pH =9, B) 2H after flushing with 4 mL of pH 9 water, C) 3H after flushing with 4 mL of pH 4 water, D) 1H after flushing with 4 mL of pH 9 water.

In Figure 6, the morphology of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> copolymer micelles adsorbed on mica has been examined by in situ soft-contact AFM. Unlike micelles in bulk solution, the adsorbed PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> copolymer micelles do not dissociate at low pH, but remain attached to the interface. We observe that (i) the adsorbed micelles seen at high pH “open” at low pH (due to protonation of the hydrophobic PDEAEMA core chains) (Figure 6 C), and (ii) the original core-shell adsorbed micelles appear to be reformed on returning to high pH (Figure 6 D).

The adsorption of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> copolymer micelles was then investigated further using contact angle measurements. First, the comparison of static contact angle (CA) of an uncoated and coated glass slide (considered as silica) allowed us to confirm that a copolymer layer was adsorbed onto the surface: A higher CA was obtained after coating at pH 9 as expected. (Figure 7).

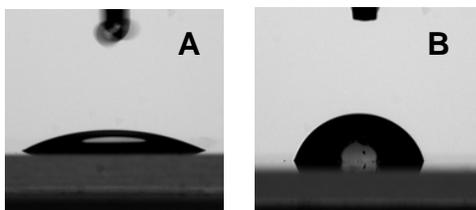


Figure 7 : Images (0.1s after deposition) of a drop of water on an uncoated glass slide (A) and on a glass slide coated with an adsorbed layer of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> (B)

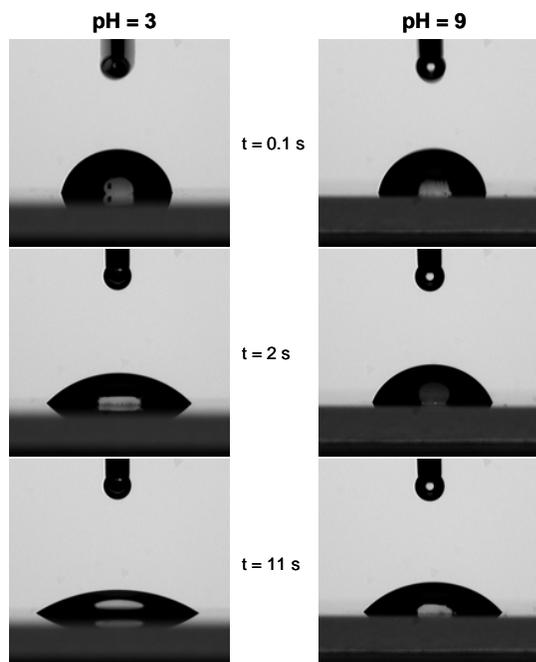


Figure 8 : Images of a drop of KNO<sub>3</sub> solution (10 mM) at pH = 3 and pH = 9 on a glass slide coated with an adsorbed layer of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub>.

The contact angles were then measured as a function of pH. Figure 8 shows images of a droplet on the coated surfaces at two pH (viz. 3 and 9) and at three times after deposition of the drop. In Figure 9, data for the contact angle as a function of pH at three times after droplet deposition are given. Clearly, the CA values tend to

increase with increasing pH. It is also noticeable that the droplet spreads slowly over the surface resulting in a reduction in the contact angle with time. These variations are directly related to changes in the morphology of the layer in agreement with our observations from the AFM images: at pH 9 a micellar morphology is seen whilst at pH 4 a “brush-like layer” is formed.

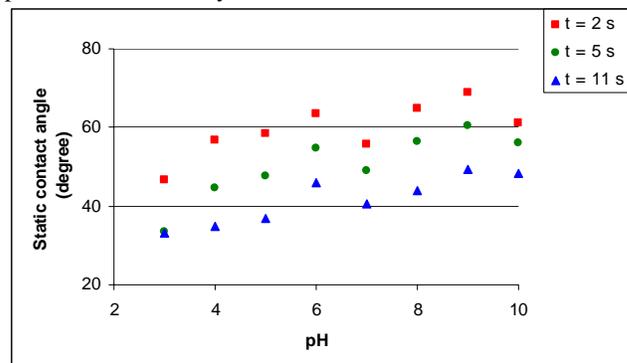


Figure 9 : Variation of the static contact angle on a glass slide coated with an adsorbed layer of PDEAEMA<sub>29</sub>-PDMAEMA<sub>95</sub> as a function of pH : (■) 2s after deposition (●) 5s after deposition (▲) 11s after deposition.

#### 4 CONCLUSIONS

The synthesis of PDEAEMA-PDMAEMA block copolymer has been successfully performed by RAFT polymerization. Characterization of copolymers in aqueous solution indicated a reversible pH-dependent unimer-micelle transition with micelles formed at pH > 7.3. The adsorbed layer showed a reversible pH-dependent morphology. Analysis of the contact angles as a function of pH showed a direct correlation with the morphological changes seen from the AFM images.

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