



# Pulsed laser studies of cationic reactive surfactant radical propagation kinetics



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## ABSTRACT

Pulsed laser polymerization coupled with size exclusion chromatography (PLP-SEC) was implemented to study the micellar radical homopropagation kinetics of cationic surfmer, polycaprolactone choline iodide ester methacrylate (PCL<sub>n</sub>ChMA with  $n = 2$  average polyester units), at concentrations of 5, 10, and 20 wt% in aqueous solutions at 25, 50, 70, and 85 °C. PCL<sub>2</sub>ChMA can propagate in both aqueous and compartmentalized phases, with the relative importance of the two reaction loci changing with temperature. As the corresponding saturated macromonomer concentration,  $[M]$ , inside the growing polymeric micelles cannot be easily determined, only the product of propagation rate coefficient ( $k_p$ ) and  $[M]$  are measured by PLP-SEC; at 25 °C, a minimum  $k_p$  of  $863 \pm 95 \text{ L mol}^{-1} \text{ s}^{-1}$  is estimated assuming bulk  $[M]$ . (Macro) monomer composition drifts for batch acrylamide (AM)/PCL<sub>n</sub>ChMA micellar copolymerizations in D<sub>2</sub>O at 50 °C are well represented by the apparent reactivity ratios  $r_{AM} = 0.31 \pm 0.03$  and  $r_{PCL_3ChMA} = 8.79 \pm 0.38$ .

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## 1. Introduction

Polyelectrolytes are unique among polymers because their ionic character allows them to participate in long-range Coulombic interactions which can be exploited for many applications [1]. In particular, cationic polyelectrolytes (i.e., polycations) find uses in diverse areas as flocculants [2,3], as anti-microbial devices [4], and in gene therapy [5]. In many cases, the charge density as well as the hydrophobic content of the polyelectrolyte are important parameters which need to be carefully designed in order to control performance [6]. The charge density along the polyelectrolyte backbone can be tuned via aqueous radical copolymerization of a cationic monomer with non-ionic hydrophilic monomers such as acrylamide (AM) [7,8], while the hydrophobic content may be adjusted via a technique known as micellar radical polymerization (MRP) [9]. In MRP, the hydrophobic monomer may be solubilized in an appropriate surfactant solution, or a reactive surfactant (surfmer) may be polymerized [10–12].

In the former version of MRP, the copolymers are produced with blocky hydrophobic microdomains whose lengths depend on the intrinsic reactivity of the hydrophobic/hydrophilic comonomers as

well as the so-called micellar effect in which the reactivity of the hydrophobic monomer is enhanced due to its compartmentalization [13]. The micellar effect extends to surfmer polymerization as surfmers form micelles which give rise to elevated polymerization rates and high molecular weight (MW) materials above their critical micelle concentration (CMC) [14], whereas polymerizations below the CMC are very inefficient [15]. The large MWs produced by surfmer MRP can be explained in part by the high local concentration of compartmentalized polymerizable groups, but also by the observation that preservation of micelle structure after polymerization is highly unlikely because the rate of surfmer exchange between micelles is much faster than the rate of radical propagation [16,17]. In other words, despite continuous nucleation and dynamic reorganization of the system, surfmer MRP is similar to emulsion radical polymerization in that a saturated monomer concentration inside the growing particle is maintained by monomer diffusion from a reservoir.

Indeed, for the MRP of cationic tail-type surfmer,  $\omega$ -methacryloyloxyundecyltrimethylammonium bromide (MUTAB), with concentration twice its CMC at 25 °C, Chatjaroenpron et al. showed that the presence of unpolymerized MUTAB micelles and a constant concentration of free aqueous MUTAB were maintained up to  $\approx 50\%$  conversion, confirming that poly(MUTAB) micelles grow at the expense of the unpolymerized ones [18]. In terms of morphology, unpolymerized and fully polymerized MUTAB micelles are

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spheroidal (i.e., geometries with long and short radii ranging roughly from 10 to 100 Å and 10 to 20 Å, respectively), while at intermediate conversions rod-like mixed polymer/monomer micelles (with length and cross-section radius ranging roughly from 200 to 3000 Å and 10 to 30 Å, respectively) coexist in dynamic equilibrium with unpolymerized micelles [18–20]. The structures of poly(MUTAB) systems are also sensitive to environmental factors, responding dynamically and reversibly to temperature, counterion, and salt addition [21]. Furthermore, as suggested by Hamid and Sherrington [22], cationic tail-type surfmers, such as MUTAB, can adopt a “looped” or “hairpin” conformation where both cationic head and polar methacrylate tail reside at the micelle/water interface. The extent to which the methacrylate group partitions to the micelle/water interface instead of the micelle core depends on conditions like temperature and counterion type [23], and it could be that its radical propagation behavior is different at the two sites. Although many recent works have been devoted to understanding the self-assembly behaviors of surfmers [21], there are currently no studies to estimate individual propagation rate coefficients ( $k_p$ ) for these intricate systems.

The pulsed-laser polymerization coupled with size exclusion chromatography (PLP-SEC) technique is the most reliable and accurate method to evaluate  $k_p$  and is described by Beuermann and Buback in comprehensive detail [24]. The product of  $k_p$  and monomer concentration,  $[M]$ , is estimated according to Eqn. (1), where  $L_i$ , determined by SEC, is a measure of the number of propagation steps of a growing macroradical that survived  $i$  dark periods during a low-conversion PLP experiment, and  $t_0$  is the time between pulses.

$$\frac{L_i}{t_0} = i \cdot k_p [M] \quad (1)$$

The IUPAC subcommittee on “Modeling of Polymerization Kinetics and Processes” has benchmarked Arrhenius parameters that describe family behavior for the bulk  $k_p$  of methyl methacrylate (MMA) and other alkyl ester methacrylates [25,26], where an increase in linear length of the ester side chain correlates with an increase in bulk  $k_p$ . However, the study of aqueous propagation kinetics is not as straightforward due to the added complexities of aqueous phase SEC analysis [27], and significant solvent effects on  $k_p$  [28]. For example, entropic reasons dictate that the  $k_p$  for non-ionized water-soluble monomers, such as methacrylic acid (MAA), increases sharply towards low monomer concentrations [29–36], while the activation energy ( $E_A$ ) of partially and fully ionized MAA decreases towards higher monomer concentrations corresponding to greater ionic strengths [37].

To date, the successful application of PLP-SEC to a cationic monomer system has not been reported. The main challenge is the ionic repulsion in the system which significantly reduces the probability of termination of growing polycations, and therefore restricts the PLP technique to a narrow range of operating conditions known as the low-termination limit (LTL) [38–40]. Thus, Kattner et al. recently developed a new technique combining a single laser initiated pulse with time resolved electron paramagnetic resonance (SP-PLP-EPR) to measure the  $k_p$  of 20 wt% [2-(methacryloyloxy)ethyl]trimethylammonium chloride (TMAEMC) in  $D_2O$ ; a value of  $3500 \text{ L mol}^{-1} \text{ s}^{-1}$  at  $60^\circ \text{C}$  was determined [41], while the corresponding  $E_A$  and pre-exponential of  $15 \pm 1 \text{ kJ mol}^{-1}$  and  $(7.9 \pm 0.5) \times 10^5 \text{ L mol}^{-1} \text{ s}^{-1}$ , respectively, were estimated using two independent treatments of conversion profiles from chemically initiated batch homopolymerizations [42]. Furthermore, although PLP-SEC has been implemented in heterogeneous systems to deduce the local styrene concentration compartmentalized in microemulsion droplets [43], latex particles [44,45], and vesicle

structures [46], PLP-SEC has not yet been applied to estimate  $k_p$  for a self-assembled reactive surfactant system. In this work, the PLP-SEC technique is applied to the cationic tail-type surfmer, polycaprolactone choline iodide ester methacrylate (PCL<sub>n</sub>ChMA), a macromonomer system with easily tunable cationic/hydrophobic content developed to produce flocculants that promote rapid settling of suspended solids and also enhance sediment dewaterability in response to hydrolytic degradation [47]. The structure of PCL<sub>n</sub>ChMA is shown in Scheme 1 alongside TMAEMC (chloride counterion) and TMAEMI (iodide counterion) which correspond to PCL<sub>n</sub>ChMA macromonomers with  $n = 0$  polycaprolactone units. Finally, with the aim of further controlling the cation density of poly(PCL<sub>n</sub>ChMA) materials, the batch copolymerization kinetics for PCL<sub>n</sub>ChMA and AM, a common comonomer in flocculants, are also investigated.

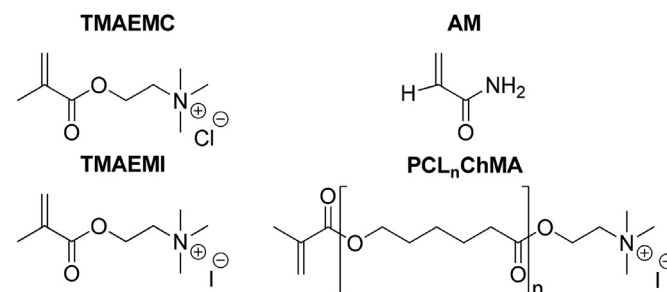
## 2. Experimental

### 2.1. Materials

$\epsilon$ -Caprolactone (CL, 97%), 2-(dimethylamino)ethanol (De, >98%), stannous octoate (Sn(oct)<sub>2</sub>, 92.5–100.0%) triethylamine (TEA,  $\geq 99.5\%$ ), dimethylformamide (DMF, 99.8%), formic acid (FA, 98.0–100%), basic alumina (Brockmann 1), methyl iodide (ICH<sub>3</sub>, 99%), acrylamide (AM,  $\geq 99\%$ ), sodium chloride (NaCl,  $\geq 99.0\%$ ), 2,2-dimethoxy-2-phenylacetophenone (DMPA, 99%), and 2,2-azobis(2-methylpropionamide)dihydrochloride (V-50, 97%) were purchased from Sigma Aldrich and used as received. Tetrahydrofuran (THF, >99%, ACP Chemicals), anhydrous diethyl ether ( $\geq 99.0\%$ , ACP Chemicals), lithium bromide (LiBr, 99+% for analysis, anhydrous, Acros), lithium phenyl-2,4,6-trimethylbenzoylphosphinate (LiTPO, synthesized by the group of Prof. R. Liska at the Institute of Applied Synthetic Chemistry, Vienna University of Technology, Austria), chloroform-d (CDCl<sub>3</sub>, 99.8% D, Cambridge Isotope Laboratories), and deuterium oxide (D<sub>2</sub>O, 99.9% D, Cambridge Isotope Laboratories) were used as received. Methacryloyl chloride (MACl, 97%, Sigma Aldrich) was distilled immediately before use. Ultrapure water was obtained from Ultrapure Water System NW Series (Heal Force Bio-Meditech Holdings, Ltd., China).

### 2.2. Macromonomer syntheses and characterizations

The syntheses of polycaprolactone 2-(*N,N*-dimethylamino)ethyl ester methacrylate (PCL<sub>n</sub>DeMA) with average  $n = 2$  and  $n = 3$  were performed according to a previously published procedure [47] modified to reduce reaction time. For the synthesis of PCL<sub>2</sub>ChMA, a catalyst/monomer mixture with molar ratio of 1:500 consisting of Sn(oct)<sub>2</sub> (35.1 mg, 86.6  $\mu\text{mol}$ ) and CL (4.94 g, 43.3 mmol) was loaded into a 50 mL sealed round bottom flask, purged with nitrogen, and then heated to  $130^\circ \text{C}$ . De (1.93 g, 21.7 mmol) was added to the catalyst/monomer mixture by syringe and allowed to react



Scheme 1. Chemical structures for (macro)monomers relevant to this work.

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