# Critical Association Concentration of Dansyl-Poly (acrylic acid) Synthetized by Redox Polymerization Followed by an Esterification in Aqueous Solution: Spectrophotometric and Tensiometric Studies

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# Abstract

In the present work, the critical concentration for self-assembly of dansyl-polyacrylic acid (DANS-PAA) in aqueous solution has been characterized by a combination of spectrophotometric and tensiometric techniques, number average molar mass, degree of polymerization, and average number of bonds were also determined. The normalized absorbance value for DANS-PAA ( $10^{-4}$  wt%) as a function of PAA concentration was at maximum below a critical self-assembly concentration (CAC) of 0.0005 g·mL<sup>-1</sup> and decreased dramatically with PAA concentration above this CAC. This supposes that upon adding more polymer, assembly occurs in a short concentration range about 0.0005 g·mL<sup>-1</sup>. Similarly, surface tension measurements for DANS-PAA decreased markedly with concentration after a threshold of around 0.0005 g·mL<sup>-1</sup>, above which it remained constant at ca. 20 dyne·cm<sup>-1</sup>. Consequently, the binary techniques produced an equivalent estimation of the CAC. Additionally, surface tension studies showed that the DANS-PAA polymer miscible with water caused surface tension to decrease by 49 % over a concentration range of 0 to 0.0014 g/mL, whereas marked reduction in surface tension (33 %) upon adding PAA, and slight decreasing (7%) was recorded upon adding acrylic acid monomer (AA) to water. Copyright © VBRI Press.

Keywords: Polyacrylic acid, dansyl-poly (acrylic acid), redox polymerization, absorbance, surface tension.

# Introduction

Polyelectrolytes such as poly(acrylic acid) (PAA) undergo to a self-association in aqueous solutions caused by exposing to stimuli like pH [1-3], temperature [4], salt concentration [2, 3, 5] and polymer concentration [3]. This aggregation occurs because of amphilic property of PAA, which has hydrophobic part (CH<sub>2</sub>-CH) has a tendency to self-associate and hydrophilc part (COOH) lets polymer dissolve in water [6]. In recent studies poly (acrylic acid) has been modified with hydrophobic groups like pyrene [1], naphthene [1], hydrocarbon and fluorocarbon end-capped poly(ethylene glycol) (PEG) macromonomers [7], or hydrophilic groups like ethylene diamine [8] and folic acid [8]. Clear majority of modified PAA polymers assemble in transient networks [6, 9] or micelle-like aggregations [6, 10]. As well known, the critical self-association-concentration (CAC) is a concentration at which polymer chains aggregations begin to form [6, 11]. Unfortunately, some modified polymers form poorly defined associations instead of compact globules [6]. Moreover, the degree of association for an amphilic polymer tend to has CAC larger than critical micellar concentration (CMC) of

simpler molecules like surfactants. This is because of increasing in polydispersity during synthesis of amphilic polymers, which means producing polymer with different chain lengths [6].

In this work, the polymerization of acrylic acid was carried out by using reduction-oxidation (redox) initiator. There are several advantages of using redox polymerization [12-14], these benefits include the polymerization to be carried out at low temperature, consequently minimizing the possibility of side reactions which may change the polymerization kinetics and the properties of the produced polymer. Additionally, large average molecular weight polymers with high yields and good polydispersity index can be obtained in a very short time [12-14]. Although redox polymerizations are rapidly done in aqueous suspension at relatively low temperatures, different kinds of redox agents, including inorganic and organic compounds, could be used for the purpose [13, 14]. When water is applied as a solvent, there are some advantages compared to organic solvents. Water is a cheap, clean and environmentally friendly solvent and chain transfer to solvent is not exist [13, 14].

In our recent work amino naphthalene sulfonic acid (AmNS) has shown to be a reliable reporter of polymer conformation in solution, and has been used in to study the aggregation of poly(acrylic acid) onto the surface of calcite [15]. This study has focused on preparing poly (acrylic acid) in aqueous solution via redox polymerization, then produced polymer was covalently coupled with dansyl groups (derivative of AmNS). In order to investigate the transition from dispersed to assembled polymer chains at different polymer concentrations, a combination of UV-vis spectroscopic and tensiometric techniques were applied.

## **Experimental**

## Materials

Propanol (Aldrich Spectroscopic grade), water (double distilled), nitric acid ( $\geq$ 97%, Fluka), potassium carbonate (99%, Aldrich), hydrochloric acid ( $\geq$ 37%, Fluka), sodium hydroxide (Fisher Laboratory grade), ceric ammonium nitrate (CAN) (97%, BDH), dichloromethane (Sigma-Aldrich), pyridine (98%, Sigma-Aldrich), dansyl chloride ( $\geq$ 97%, Alfa Aesar,), methanol (Sigma), and acrylic acid (AA) (99%, Aldrich), used as received, without any further purification.

# Redox polymerization of acrylic acid in aqueous solution

Redox polymerization of acrylic acid was carried out by taking clean round bottom flask containing 100 mL of distilled water used as a solvent in the reaction. A definite amount of ceric ammonium nitrate and nitric acid was added to the reaction flask followed by dropwise addition of monomer with continuous stirring of the reaction mixture. The reaction was done at certain reaction time and temperature. Typical conditions of time, temperature, pH, ceric ammonium nitrate, nitric acid and monomer concentration were worked out to acquire good homo polymer yield. The polymer formed was precipitated by adding enough from propanol. The sample was then dried in hot air oven at 60°C to a constant weight. A suitable mechanism has been proposed in **Scheme 1**.



Scheme 1. Redox Polymerization of acrylic acid initiated by Ce4+.

## Synthesis of Dansyl Functional Poly(acrylic acid) (DANS-PAA)

Dansyl groups were covalently attached as side groups by esterification between dansyl chloride and carboxyl functional groups of PAA, as shown in **Scheme 2**:



**Scheme 2.** General procedure for the synthesis of dansyl functional poly (acrylic acid).

#### **Characterization Techniques**

#### Viscometry

Values for the efflux time of monomer and polymer solutions were measured by Ostwald glass capillary viscometer, then viscosity values were expressed in centipoise units (cp). The viscometer was calibrated at room temperature by using double distilled water as a working fluid.

## Yield calculations

The polymer yield was obtained by expressing the mass of end material as a relative percentage of the monomer, as follows:

Polymer yield% = 
$$\frac{\text{weight of isolated polymer (g)}}{\text{weight of monomer (g)}} \times 100$$
 (1)

#### Ultraviolet-visible spectroscopy (UV-vis)

UV-vis spectra were recorded with a Perkin–Elmer spectrophotometer. The scan was done from 600 nm to 200 nm with a scan speed of 100nm/min and slits were set at 2 nm. Dansyl chloride at different concentrations in methanol, whereas functionalized polymer solutions at  $10^{-1}$  and  $10^{-4}$  wt% in distilled water were prepared and measured at room temperature.

#### Surface tension measurements

The surface tension  $(\gamma)$  of monomer and polymer solutions were determined by using the capillary-rise method. The tensiometer was calibrated at room temperature by using double distilled water as a working fluid. The glass tube was 10 cm long and of 1 mm inside diameter. The lower end of this tube was placed in the sample liquid contained in a beaker. Stainless steel measure was similarly attached on the plastic board behind the glass tube. Hence, the location of the meniscus of the sample was read.

### **Results and discussion**

Essential requirements for the determination of number average molar mass  $(\overline{M}_n)$  for PAA by UV-vis spectroscopic technique is the attachment of a chromophore like dansyl and getting wavelength scan in which, the chromophore group has distinguishable peaks compared with native polymer. Herein as shown in Fig. 1, the prerequisites are fulfilled since DANS-PAA spectra have unique bands compared to PAA, two peaks were displayed for DANS-PAA at 257 nm and 339 nm. The 257 nm peak was discarded form the calculation because there was an obvious influence of the PAA band, which has a peak at 251 nm could be assigned to the carbonyl group of PAA. Hence, only the absorbance values at 339 nm were considered for the attached chromophore analyses based on UV-vis spectroscopy, its worthy to note that the second peak (339 nm in DANS-PAA) was shifted to longer wavelength compared to DANS alone in solvent which has a maximum absorbance at 325 nm for the second peak (see Fig. 2), this supports that a covalent attachment might occurred between the chromophore and polymer chain. Additionally, these analyses assume that the extinction coefficients of the DANS group in the PAA is close to the extinction coefficients  $\varepsilon$  of the DANS chromophore alone. Another requirement is the conservation of DANS group in the polymer chain. Unsuccessful attachment will lead to an artificially high M<sub>n</sub> value.



**Fig. 1.** UV-vis spectra of poly (acrylic acid) (PAA) and dansyl labelled poly (acrylic acid) (DANS-PAA) in 10<sup>-1</sup>wt% concentration in water. The arrow designates the position of the maximum wavelength ( $\lambda_{max}$ ) in the UV-vis spectrum of the DANS chromophore, which is used in the study.



Fig. 2. UV-vis spectra of dansyl chloride in methanol at different concentrations.

The concentration of DANS groups  $C_{DANS}$  in  $10^{-1}$ wt% DANS-PAA solution was calculated from the measured absorbance A at 339 nm according to the following:

$$C_{DANS}(\frac{mol}{L}) = \frac{A}{\varepsilon b}$$
(2)

where *b* is the bath length of the cell, equal to 1 *cm* and  $\varepsilon$  is extinction coefficient of the DANS group, which can be determined from the Beer-Lambert's law for the calibration curve as shown in **Fig. 3**, a typical linear relationship was plotted with slope equal to 0.001122 x 10<sup>6</sup>, by applying in equation (2) that gives an extinction coefficient equal to 1122 L mol<sup>-1</sup>·cm<sup>-1</sup>, and C<sub>DANS</sub> equal to 3.1 x 10<sup>-5</sup> mol L<sup>-1</sup>, which can be expressed in g L<sup>-1</sup> by using the following equation:

$$C_{DANS}\left(\frac{mol}{L}\right) x M_{DANS} = C_{DANS}\left(\frac{g}{L}\right)$$
(3)





Fig. 3. Beer-Lambert's law of DANS at different molar concentration in methanol. ( $\lambda_{max} = 325$  nm).

The concentration of poly (acrylic acid) repeat units in the solution can be calculated from equations (4) and (5). The molar ratio of polymer repeat units to DANS groups is the number average degree of polymerization of the polymer, <DP>;

$$C_{Polymer}\left(\frac{g}{L}\right) - C_{DANS}\left(\frac{g}{L}\right) = C_{Repeat}\left(\frac{g}{L}\right)$$
 (4)

$$\frac{C_{Repeat}\left(\frac{g}{L}\right)}{M_{Repeat}} = C_{Repeat}\left(\frac{mol}{L}\right)$$
(5)

$$\frac{C_{Repeat}\left(\frac{mol}{L}\right)}{C_{DANS}\left(\frac{mol}{L}\right)} = < DP >$$
(6)

The number average molar mass was calculated according to following equation;

$$\frac{n M_{Repeat}}{2} = \bar{M}_n \tag{7}$$

$$n = 2 < \mathrm{DP} > \tag{8}$$

where (n) is the average number of bonds.

The degree of functionalization for the synthesized DANS-PAA was expressed in mol% of the dansyl group, and was calculated by the following equation:

$$(mol\%)_{DANS} = \frac{C_{DANS}}{C_{DANS} + C_{Repeat}} \times 100$$
(9)

The values of the number average molar mass, the degree of polymerization, and viscosities ( $\eta$ ) are listed in **Table 1**. The calculated results show that the  $\overline{M}_n$ ,  $\eta$  in cp, <DP>, and *n* for the synthesized polymer are greater than those of acrylic acid monomer. This indicates that the redox polymerization for the monomer was successively carried out.

Table 1. Shows the number average molar mass and related parameters for synthetized polymer and its monomer.

System	$\overline{M}_{n}$ (g/mol)	η (cp)	<dp></dp>	n
DANS-PAA polymer (mol%) <sub>DANS</sub> =0.2 Yield: 75%	31988	3000	444	888
AA monomer	72	1.3	0	0

To confirm the self-assembly of DANS-PAA upon adding more amount of PAA the UV-vis spectra were performed using the normalized absorbance value for DANS-PAA at fixed concentration of 10<sup>-4</sup> wt% in aqueous system at natural pH value (Fig. 4). After addition of PAA in DANS-PAA solution, the maximum absorbance at 339 nm was recorded. Significant aggregation of the PAA to the DANS-PAA occurred (Scheme 3), which confirmed the self-assembly of polymer through the carboxyl groups present in its chain. The degree of assembled polymer was determined from the decrease in the absorbance value after the DANS-PAA was exposed to the PAA solution. The absorption was at maximum below a critical self-assembly concentration (CAC) of 0.0005  $g \cdot mL^{-1}$  and decreased sharply with PAA concentration above this CAC. This presumes that upon adding more polymer, assembly occurs in a short concentration range about  $0.0005 \text{ g}\cdot\text{mL}^{-1}$ , since DANS-PAA is surrounded by hydrophobic domain (PAA) leads to a decline in DANS absorbance, which is hydrophilic chromophore.



Fig. 4. The normalized absorbance value for DANS-PAA ( $10^{-4}$  wt%) as a function of PAA concentration.



Scheme 3. Critical self-assembly concentration (CAC) of DANS-PAA upon adding PAA.

The surface tension ( $\gamma$ ) of polymer solution was determined by using the capillary-rise method, one advantage of this method is the absence of weightiness of polymer solution, which is not possible for measuring tiny quantity of polymers. Mathematically ( $\gamma$ ) is given by the following expression [16]:

$$\gamma = \frac{1}{2}\rho gr(h + \frac{1}{3}r) \tag{10}$$

where,  $\gamma$  is the surface tension of polymer solution (dyne/cm),  $\rho$  is the density of polymer solution (g/cm<sup>3</sup>), g is the acceleration due to the gravity (cm/s<sup>2</sup>), r is the radius of capillary, and h is the height of polymer solution in capillary (cm). Since the surface tension of a polymer solution at fixed concentration is controlled by thermodynamical parameters [16], and most of polymer solutions revealed a decrease in surface tension with increasing temperature [17], in this work we have determined surface tensions at room temperature. The pure water obtained by double distillations assayed at 60.00 dyne/cm, which is in agreement with literature, has been found to equal 60.22 dyne/cm [18]. Surface tension of AA, PAA, DANS-PAA solutions (solvent distilled water) of different concentration for three materials are recorded and shown in Fig. 5. It can be noted that, when the concentration of all materials solution increases, the surface tension value decreases over the studied range from 0.00 to ~0.0014 g/mL. While miscible with water acrylic acid behaves as a surfactant causing surface tension to slightly decrease by 7% when the concentration of monomer in solution reached 0.0014 g/mL and according to surface tension measurements, critical micelle concentration (CMC) therefore occurs slightly above the concentration of ~0.0010 g/mL determined by the gradient point of the tensiometric curve (Fig. 5). Whereas PAA behaves better than AA when it was added to water, causing surface tension to decrease by 33% over a concentration range of 0.00-0.0014 g/mL. Interestingly, when adding DANS-PAA to water caused in a marked reduction in the surface tension of water, since the percent of decrease reached to 49%. However, this decline in surface tension could be explained in terms of hydrogen bonding between solutes (AA, PAA, or DANS-PAA) and their solvent (double distilled water). All three solutes bearing carboxyl groups (-COOH), on one hand these moieties can form hydrogen bonding with water molecules which in turn lead to a decrease in surface tension, on the other hand self-aggregation of three solutes could occur as a result of hydrogen bonding between solutes with each other, but this kind of assembly depending on the solute concentration, it is known as critical concentration. Through adding PAA into water, the PAA--H-OH cluster attracts neighbor water--water cluster. Due to the hydrogen bonding in PAA--H-OH cluster is weaker than that of water cluster, PAA molecules can easily separate from surrounding water molecules and immediately migrate to surface of solution. The accumulation of PAA on the surface results in additional positive surface tension values and hence the surface tension of PAA solution is decreased. Whereas, larger reduction in surface tension upon adding DANS-PAA could be attributed to hydrophobic naphthalene ring for dansyl chromophore which tend to aggregate in the surface of solution instead of interior solution. Furthermore, decreasing the surface tension upon adding more solute could occurs because of weaker interaction between solute molecules compared with solutes present in the surface.



**Fig. 5.** Surface tension of DANS-PAA, PAA, and AA in aqueous solution, measured by capillary-rise tensionmetry, as a function of concentration. Lines are guides for the eye to calculate the critical concentration for self-assembly.

### Conclusion

The sharp decrease of water surface tension via modified polymer (DANS-PAA) is promising as compared to other surface-active agents. The measured surface tension values of AA and PAA solutions caused in decrease of water surface tension by 7 % and 33% respectively over the range of solute concentration from 0.00 to approximately 0.0015 g/mL at room temperature and natural pH. In contrast, the surface tension values of DANS-PAA solutions showed a significant decrease from a value of 60 dyne/cm at zero concentration (pure water) to a value of ~30 dyne/cm at ~0.0015 g/mL, approaching an asymptotic value of 65.2 dyne/cm at higher concentration.

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#### Author's contributions

Conceived the plan: Fateh, Abdelkader; Performed the experiments: Nada, Naziha; Data analysis: Fateh, Mansour; Wrote the paper: Fateh. Authors have no competing financial interests.

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