



# Dissociation and thermal characteristics of poly(acrylic acid) modified pluronic block copolymers in aqueous solution



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## ABSTRACT

The effect of salt on the dissociation behavior of a Pluronic-polyacrylic acid penta-block copolymer (P85PAA65) was examined. The average Gibbs energy corresponding to the energy for extracting a proton from P85PAA65 copolymer chains decreased with increasing NaCl concentration, suggesting that the addition of salt favors the dissociation process. A fluorescence study showed a two-step dissociation in which the formation of polymer complexes composed of a hydrophobic core surrounded by a hydrophilic shell was observed at pH 3.7, where the hydrodynamic radius ( $R_h$ ) of the micellar structure increased from 145.6 to 302 nm due to coulombic repulsion of slightly charged PAA segments. As a consequence, the pyrene's first and the third vibronic peaks ( $I_1/I_3$ ) ratio increased from 1.408 to 1.580, indicating a less hydrophobic or loose-coiled conformation compared to at a higher pH. At a pH of 7.22, the dissociation of the P85PAA65 copolymer was complete, yielding a dissociated polymer chain with apparent hydrodynamic radius ( $R_h^{app}$ ) of about 3.2 nm. A reduction of the critical micelle temperature (CMT) attributed to the hydrogen bonding between Pluronic and PAA segments was observed.

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## 1. Introduction

There is an increasing need for the development of responsive polymer systems since intelligent self-assembled systems have become attractive systems for a wide range of applications [1–3]. Many responsive polymer systems have been investigated, however biocompatible polymers, such as the Pluronics are increasing being explored for many applications. Pluronic block copolymers (PEO-PPO-PEO) modified with poly(acrylic acid) at both ends have been described previously [4]. In the solid state, FT-IR spectra indicate the formation of intra- or inter- H-bonding within the block copolymers. The complex formation affects the miscibility and glass transition temperature of PAA-modified Pluronic block copolymer. In an aqueous medium, the formation of hydrogen-bonded interpolymer complexes between a proton donor, for instance poly(acrylic acid), and a proton acceptor such as poly(ethylene oxide) has been investigated [5–8]. The H-bonding association between the carboxylic groups of the polyacid and the ester

oxygen of PEO is a cooperative process [6], leading to the formation of stable, compact intermolecular complexes; it is also a pH-dependent process [9–12] in which the complex formed precipitates at pHs lower than 3.0–3.5, and dissociates at pH values higher than 4–5. A soluble intermolecular complex was observed in the pH range 3.0–3.5. Recently, two research groups have reported studies on the interpolymer association between Pluronic copolymers and PAA [13,14], where they found that the formation of hydrogen bonding between the ether groups on the poly(propylene oxide) and poly(ethylene oxide) and carboxyl of PAA decreased the dissolution rate of the Pluronic/PAA interpolymer complex.

Lu et al. studied the effect of PAA on the phase transition behavior of hydroxypropylcellulose (HPC) [15]. They observed that the formation of H-bonded interpolymer complexes between PAA and propylene oxide on hydroxypropylcellulose limited the accessibility of water to the polymer chains, thereby increasing the hydrophobicity of HPC, leading to a drastic reduction in the lower critical solution temperature (LCST) of the nonionic polymer. Temperature-dependence micellization is one of the characteristics of Pluronic block copolymers. The impact of adding polyethylene-oxide of varying chain length on the gelation of Pluronics F127 was recently reported by Chen and co-workers [16]. It was found

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that the addition of PEO lowered the critical micelle temperature of F127.

It is generally believed that the dehydration of the hydrophobic PPO block with increasing temperature is responsible for micelle formation because high temperature diminishes the hydrogen bonding between PPO and water [17–21]. The structure of PEO-PPO-PEO copolymer micelles is well described by a core–shell model in which the dehydrated PPO core is stabilized by the hydrated PEO blocks at the micellar surface [22]. The critical micelle temperature (CMT) and critical micellization concentration (CMC) decrease with increasing molecular weight or PPO content. When Pluronic P85 is modified with PAA, the formation of inter- or intra-molecular H-bonded complexes may occur in aqueous solution, and they alter the temperature sensitivity of the modified Pluronic block copolymer. In this paper, the dissociation and temperature-dependent micellization of modified Pluronic block copolymers was studied. The critical micelle temperature (CMT) of modified Pluronic block copolymers with PAA was measured by fluorescence spectrometry.

## 2. Experimental

### 2.1. Materials

Pluronic P85 was obtained from BASF (Mount Olive, NJ). The details of the synthesis of the block copolymer and its characterization were described previously [23]. The composition of the block copolymer has the following characteristics; AA:EO:PO = 65:54:39, molecular weight from NMR: 9600 g/mol; PDI = 1.15; carboxylic acid content: 6.45 mmol/g. The GPC trace is shown in Figure S1. Figure S2 shows the FT-IR spectra, which confirmed the presence of carboxyl groups and indicated the formation of intra- or inter- H-bonding of PAA and PEO segments. The absorbance bands in the 1650–1700 and 1100 cm<sup>-1</sup> regions corresponded to the COOH in PAA and the C–O–C stretching in Pluronic. The polymer is designated as P85PAA65, where the number "65" corresponds to the repeating unit of AA.

### 2.2. Potentiometric titration

The ion-exchange capacity of P85PAA65 block copolymer was obtained by titrating 0.1 wt% polymer solution with 1 M standard NaOH solution at 25 °C under a constant stirring. An ABU93 Tributret Titration system equipped with Radiometer pHG201 pH glass and Radiometer REF201 reference electrodes was used for pH measurement. One minute of lag time was allowed between two dosages to ensure that the reaction had reached equilibrium.

### 2.3. Transmission electron microscope (TEM)

Transmission electron microscopy was used to visualize the morphology and size of P85PAA65 complexes in dilute solution, performed on a JEOL JEM-2010 electron microscope at an acceleration voltage of 120 kV. The sample was prepared on a 400 mesh copper grid precoated with a carbon film and stained with phosphotungstic acid (0.1 wt%, ethanol) or osmium tetroxide (OsO<sub>4</sub>) (2.5 wt% in 2-methyl-2-propanol). The copper grid was dried overnight at room temperature prior to the measurement.

### 2.4. Fluorescence spectrophotometry

The micellization behavior of the P85PAA65 block copolymer was studied using fluorescence spectrophotometry. All fluorescence spectra were recorded on an AMINCO-Bowman series 2 spectrometer (Thermo Electron Corporation, USA) in a steady-state

mode with 4 nm band-pass for excitation and 2 nm band-pass for emission. The fluorospectrometer was equipped with a standard thermostated cuvette compartment, flash lamp, detector (PMT), and excitation/emission monochromators. The operation wavelength range was 220–850 nm, with an accuracy of about ±0.5 nm and reproducible to about ±0.25 nm. Pyrene was used as a probe and prepared at 0.1 mM in acetone as a stock solution. Six μL pyrene stock solutions were added to pre-dried test tubes, most of the acetone was evaporated in a chemical hood at room temperature. Then 1 ml prepared polymer solution was added to the same test tubes, resulting in a pyrene concentration of 0.6 μM in the sample solutions, and equilibrated overnight at room temperature. For the CMT measurements, the samples were allowed to equilibrate for about 1 h at a given temperature and then transferred to 0.5 ml quartz cuvettes for measurement. All samples were excited at 337 nm, and fluorescence spectra were recorded over the range 360–430 nm. The polarity of the pyrene microenvironment was estimated from the value of I<sub>1</sub>/I<sub>3</sub>, the ratio of intensities of the first (373 nm) to the third (384 nm) vibronic peaks in the emission spectra of the monomer pyrene.

### 2.5. Dynamic light scattering

Dynamic light scattering measurements were performed on a Brookhaven laser light scattering system (Brookhaven BIS200). The equipment consisted of a BI-200SM goniometer (Version 2.0), BI-9000AT digital correlator and supporting accessories and analysis software. The goniometer system included focusing optics, a rotating arm, detector optics, detector, neutral density filter, beam focus, sample holder, and a high voltage power supply for the detector. The light source included a power adjustable vertically polarized 350 mW 488 nm argon-ion laser. The data obtained from the DLS measurement were the correlation functions represented by either the G<sub>2</sub>(t) or g<sub>2</sub>(t) function. The REPES Inverse Laplace Transformation routine supplied with the GENDIST software was used to analyze the DLS results. Stock solutions of P85PAA65 (1 wt %) block copolymer were prepared in 10 mM PBS in an ice bath and stored at 4 °C. The sample solutions (0.1 wt%) for DLS study were prepared from a stock solution and adjusted to the required pH by the addition of 5 M NaOH solution. The sample solutions were placed into a glass test tube and centrifuged (3000 rpm, 10 min) to remove dust that may have been present in the test solutions. We have chosen centrifugation as a more efficient method to remove dust particles over ultra-filtration prior to DLS measurements as ultra-filtration may remove some larger polymer aggregates.

## 3. Results and discussion

### 3.1. Dissociation behavior of P85PAA65 in aqueous solution: potentiometric titration studies

The degree of neutralization, α, of carboxylic groups is defined by:

$$\alpha = \frac{[\text{BASE}] + [\text{H}^+] - [\text{OH}^-]}{C_{\text{COOH}}} \quad (1)$$

Here, [BASE], [H<sup>+</sup>] and [OH<sup>-</sup>] are the molar concentrations of added NaOH, free hydrogen ion, and hydroxide ion, respectively. C<sub>COOH</sub> is the total concentration of carboxylic groups. The hydrogen and hydroxide ion concentrations were calculated from the measured pH. The negative logarithm of the apparent dissociation constant of protons from carboxyl groups (pK<sub>a</sub>) is related to the pH and degree of neutralization through the Henderson–Hasselbalch equation;

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