



# Photophysical evaluation of synergism from critical micelle temperature of mixed triblock polymer micelles

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## Abstract

The critical micelle temperatures (*cmt*) of binary mixtures of triblock polymer (TBP) of poly(ethylene oxide) block poly(propylene oxide) block poly(ethylene oxide) (L64, P103, P84, P104) with different PPO/PEO ratios were determined employing the fluorescence measurements. The photophysical properties of pyrene due to its quenching as well as excimer formation in the interior of the mixed TBP micelles were studied and explained on the basis of stability of the mixed micelles. It was observed that the mixed micelle formation between the unlike components of P103+L64 and P103+P84 mixtures formed due to the attractive interactions and which raised from the mutual compatible arrangement among the unlike TBP monomers in the mixed state so as to minimize the steric hindrances. The results were fully supported by the viscosity measurements.

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**Keywords:** Triblock polymers; Critical micelle temperature; Mixed micelles; Fluorescence measurements

## 1. Introduction

Poly(ethylene oxide) block poly(propylene oxide) block poly(ethylene oxide) (PEO–PPO–PEO) triblock polymers (TBP) are known to have micelle formation with respect to the variation of temperature. At a particular temperature where this micelle formation occurs is known as critical micelle temperature [1–8] (*cmt*), an analogous term used for this purpose to that of critical micelle concentration [4–8] (*cmc*) where micelle formation occurs due to a change in concentration. Although, most of the TBP's also show *cmc* process quite clearly, the presence of *cmt* in such polymers is relatively much clear and significant. At a particular concentration, an increase in the temperature leads to a sudden dehydration of poly(propylene oxide) (PPO) blocks which have relatively much weaker electrostatic interactions with water molecules in comparison to that of poly(ethylene oxide) (PEO). This process drags the PPO groups away from water and gathered them in the centre of an aggregate surrounded by more hydrophilic PEO groups. This leads to a conventional micelle type assembly with predomi-

nantly hydrophilic groups (PEO) arranged at the periphery while hydrophobic ones (PPO) constitute the core [1–3,9–15]. Such a transition is quite significant and occurs within a narrow temperature range.

Several techniques [5,16] have been applied to determine the *cmt* while pyrene fluorescence spectroscopy is considered to be more useful due to its much better accuracy. A much lower pyrene concentration (less than  $10^{-6}$  M) is sufficient to detect this change which does not influence the overall micelle formation process.

Though, several studies [5,16–19] have been reported on the *cmt* for various TBP's little is known about the mixed *cmt* behavior of binary TBP mixtures. Since TBP's are categorized in the category of nonionic polymeric surfactants, therefore, ideal mixing is generally expected in the TBP–TBP mixed systems. Recently, we have observed [20] that it is not always true, and the binary mixtures of TBP's do lead to a nonideal mixing when there is a significant difference between their molecular weights or hydrophobic/hydrophilic (PPO/PEO) ratio. This actually we evaluated from the mixed *cmc* values. However, *cmt* of TBP's is considered to be having more relevance as far as their shelf life under varying temperatures is concerned. This is due to the fact that most of the industrial products in the cosmetic industry consist of more than one TBP component where a basic under-

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standing on the nature of their mixed *cmt* values becomes quite important. At this end, we have selected some TBP binary mixtures on the basis of their different PPO/PEO ratios to evaluate their mixed *cmt* behavior.

## 2. Experimental

### 2.1. Materials

The TBP used in this study have the general formula  $H(-OCH_2CH_2-)_n[-OCH(CH_3)CH_2-]_m(-OCH_2CH_2-)_nOH$ . Table 1 lists the molecular specifications of various TBP used in the present study and all the components have been used without further purifications. Pyrene was obtained from Aldrich and was used as received. Water was purified by deionization followed by double distillation. All solutions were prepared by mass within the accuracy of  $\pm 0.01$  mg. The mole fractions were accurate to  $\pm 0.0001$  units.

### 2.2. Sample preparation

Stock solutions of different pure TBPs have been made in pure water by keeping the total concentration of each TBP =  $5 \times 10^{-4}$  mol dm<sup>-3</sup>. The change in the concentration has drastic effect on the *cmt* of TBP. For instance, increase in the concentration leads to a large decrease in *cmt* [5]. We prefer to keep the TBP concentration constant so that concentration effect can be eliminated and only temperature effect could be studied. These stock solutions were then mixed in different proportions to make binary combinations covering whole mixing range. The mole fractions of each component of various such binary mixtures have been expressed only on the solute basis.

### 2.3. Methods

#### 2.3.1. Fluorescence measurements

A constant amount of pyrene ( $2.0 \times 10^{-5}$  mol dm<sup>-3</sup>) has been maintained in all solutions. Fluorescence spectra of pyrene were obtained using Hitachi F-2500 fluorescence spectrophotometer, at an excitation wavelength of 334 nm. The intensities  $I_1$  and  $I_3$  were measured at the wavelengths corresponding to the first and third vibronic bands located at ca. 373 and 384 nm, while  $I_{exc}$  is measured at 470 nm. The ratios  $I_1/I_3$  of pyrene as a function temperature were used to directly determine the *cmt*. The desired temperature was maintained by circulating the

thermostated water by using Julabo F25 thermostat within the uncertainties of  $\pm 0.01$  °C.

#### 2.3.2. Viscosity measurements

The efflux times of binary mixtures of TBP solutions have been determined with the help of Ubbelohde type suspended level capillary viscometer sealed in a glass jacket to circulate the thermostated water at 45 °C. The efflux time was kept long to minimize the need for applying the kinetic corrections to the observed data. Each experiment was carried out after giv-

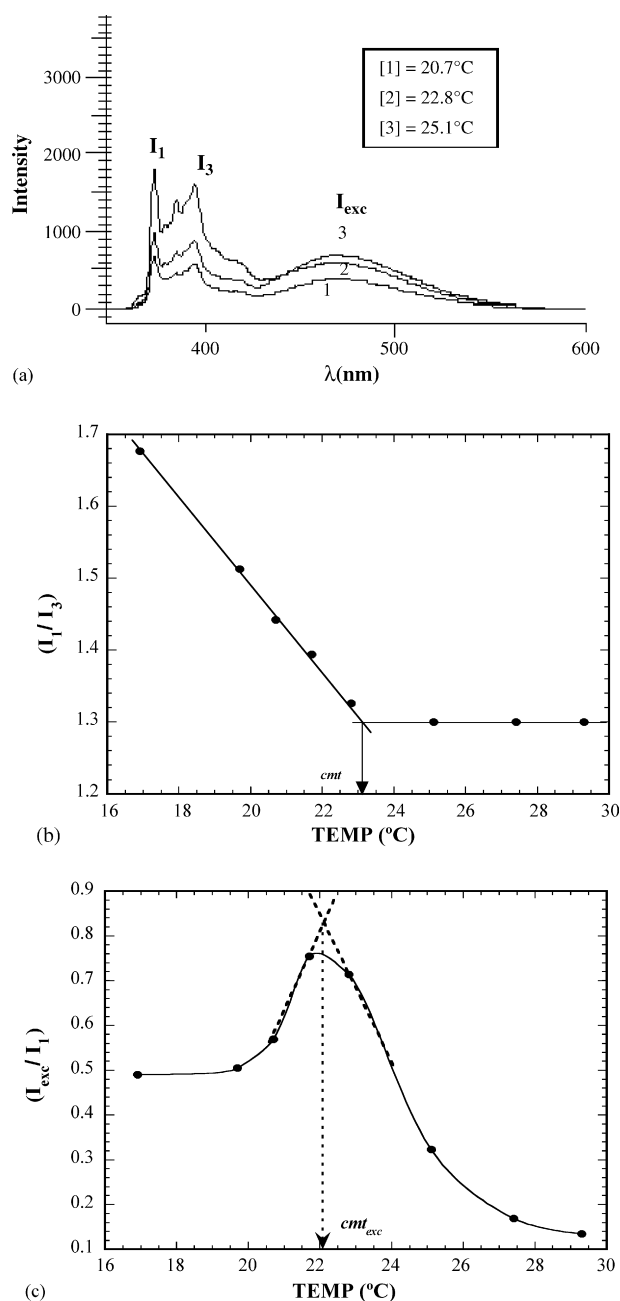


Table 1  
Molecular characteristics of PEO–PPO–PEO triblock polymers

TBP	General formula	Hydrophobic/ hydrophilic ratio	MW
L64	(EO) <sub>13</sub> (PO) <sub>30</sub> (EO) <sub>13</sub>	1.52	2900
P103	(EO) <sub>17</sub> (PO) <sub>60</sub> (EO) <sub>17</sub>	2.32	4950
P84	(EO) <sub>19</sub> (PO) <sub>43</sub> (EO) <sub>19</sub>	1.49	4200
P104	(EO) <sub>18</sub> (PO) <sub>58</sub> (EO) <sub>18</sub>	2.12	5900

Fig. 1. (a) Pyrene emission spectrum at various temperatures of [P103] =  $5 \times 10^{-4}$  mol dm<sup>-3</sup>: [1] 20.7 °C, [2] 22.8 °C, [3] 25.1 °C, where  $I_1$ ,  $I_3$ , and  $I_{exc}$  are the intensities of first, third, and excimer bands of pyrene. (b) Variation of the pyrene intensity  $I_1/I_3$  ratio with temperature for pure P103. (c) Variation of the pyrene intensity  $I_{exc}/I_1$  ratio with temperature for pure P103.

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