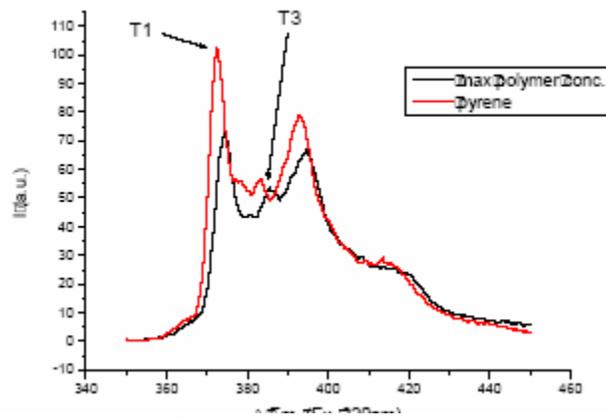


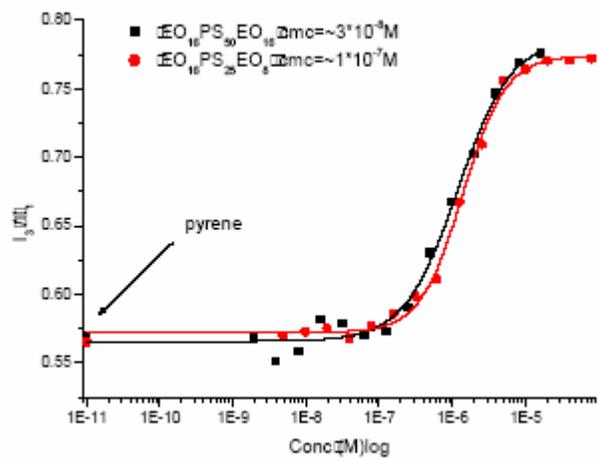
The CMC for two triblock copolymers ( $\text{EO}_{16}\text{PS}_{50}\text{EO}_{16}$  and  $\text{EO}_{16}\text{PS}_{25}\text{EO}_8$ ) was measured using the standard pyrene method. Pyrene is a hydrophobic fluorescent dye, which has characteristic absorbance and emission bands. The latter are subject to fluctuations in wavelength position and intensity depending on the polarity of the environment that surrounds pyrene molecules. When in the presence of micelles, pyrene tends to segregate in the hydrophobic cores changing the ratio of the T1 and T3 emission bands intensities. The change of this ratio with surfactant concentration occurs rapidly at the CMC when pyrene passes from the free form in water to the oil-phase confined state.

In Figure 1, the characteristic emission bands for pyrene in water (in absence of surfactant) and for pyrene with the highest polymer concentration measured are reported.

When pyrene is present in a hydrophobic non-polar environment the intensity of T1 tends to decrease and the ratio  $I_3/I_1$  increases suddenly.



**Figure 1** Characteristic emission bands for pyrene in water and in presence of aggregates from PPSPEG block copolymer. The shift and change in intensity of the T1 and T3 bands are related to the change in the polarity of the environment in which pyrene molecules are located.



**Figure 2** The increase of the ratio between the intensities of the characteristic emission bands of pyrene vs. polymer concentration. The CMC values were extrapolated from the fitted data at the point where  $I_3/I_1$  increases.

The change of the ratio  $I_3/I_1$  vs. concentration for two triblock copolymers is shown in Figure 2. The CMC values are extrapolated from the sigmoidal fit of experimental data. Such low values, in the order of  $10^{-7}$  M, are in agreement with block copolymer architecture and reflect the high hydrophobicity of the PPS block.