such properties as the surface tension, electrical conductivity, osmotic pressure, interfacial tension, or light scattering as a function of concentration, have been used for this purpose (Kakamura et al., 1976; Astafieva et al., 1993; Lieberman et al., 1996). However, for polymeric micelles, the CMC is generally too low to be determined by such methods. Light scattering is widely used for the determination of the molecular weight, size, shape, and aggregation number of micelles. However, the onset of micellization can be detected only if the CMC falls within the sensitivity of the scattering method that is rarely the case for polymers in water (Astafieva et al., 1993; Jones and Leroux, 1999). GPC under aqueous conditions can be employed since single chains and micellar chain fractions of copolymers exhibit different elution volumes (Weissig et al., 1998a,b).

CMC can also be determined from the change in the spectral characteristics of some dye probes added to the surfactant solution. A preferred method to determine the CMC involves the use of fluorescent probes (Turro and Chung, 1984; Wilhelm et al., 1991; Astafieva et al., 1993), among which pyrene is the most widely used. Pyrene is a condensed aromatic hydrocarbon that is highly hydrophobic and sensitive to the polarity of the surrounding environment (Kalyanasundaram and Thomas, 1977). Below the CMC, pyrene is solubilized in water, a medium of high polarity. When micelles are formed, pyrene partitions preferentially toward the hydrophobic domain afforded by the micellar core and thus, experiences a nonpolar environment (Kalyanasundaram and Thomas, 1977). Consequently, numerous changes such as an increase in the fluorescence intensity, a change in the vibrational fine structure of the emission spectra and a red shift of the (0,0) band in the excitation spectra, are observed. The apparent CMC can be obtained from a plot of the fluorescence of pyrene, the I1/I3 ratio from the emission spectra or the I333/I338 ratio from the excitation spectra, against concentration. A major change in the slope indicates the onset of micellization (Kalyanasundaram and Thomas, 1977) (Figure 13.23). The I1/I3 ratio is the intensity ratio between the first and third highest energy emission peaks and is measured at a constant excitation wavelength and variable emission wavelengths corresponding to I1 and I3. Some claim that I1/I3 ratio should be reserved for evaluation of polarity since it is affected by the wavelength of excitation and may result in an erroneous CMC (Astafieva et al., 1993). Thus, CMC may be better ascertained by the I333/I338 ratio (Astafieva et al., 1993; Shin et al., 1998). The CMC determined with fluorescence techniques

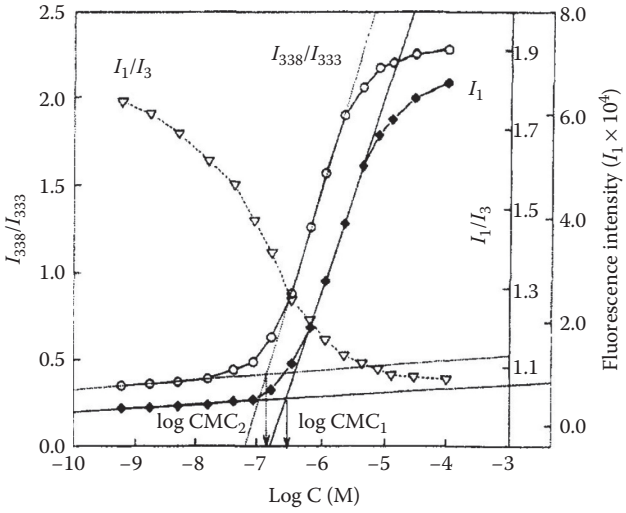

FIGURE 13.23 Plots of the fluorescence intensity I_1 and intensity ratios I_1/I_3 (from pyrene emission spectra) and I_{333}/I_{338} as a function of PST-*b*-poly(sodium acrylate) concentration. Values of CMC_{app} are indicated by arrows. (Reprinted with permission from Astafieva, I. et al., *Macromolecules*, 26, 7339–7352, 1993. Copyright 1993 American Chemical Society.)