Determination of the Critical Micelle Concentration of Block Copolymer Micelles by Static Light Scattering

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ABSTRACT: A method is proposed for the determination of the critical micelle concentration (cmc) of block copolymer micelles from static light scattering measurements, which is based on a recent model of micellization of block copolymers. The method considers the polydispersity of the block copolymers, the variation of the total single chain concentration with total concentration, and the relationship between the cmc and the length of the insoluble block. One family of block ionomers, polystyrene(660)-*b*-poly(sodium acrylate) with a low polydispersity index and ionic block lengths varying from 2.6 to 14 units, was investigated by light scattering near the cmc in THF. For this system, which had a relatively narrow molecular weight distribution and which showed a weak dependence of the cmc on the insoluble block length, it was found that the cmc values could be evaluated both by the present proposed extrapolation method and by the Debye equation. However, for polystyrene(470)-*b*-poly(4-vinylpyridine)(52) in toluene, where the dependence of the cmc on the block length is stronger, the Debye equation was not an adequate representation of the system while the proposed method was. Simulated light scattering curves for polystyrene-*b*-polyisoprene in *n*-hexadecane were calculated for various distributions for the insoluble block length. It was found that for monodisperse samples the Debye equation gave a good fit, while for broad distributions the Debye equation did not describe the $Kc/R(0)$ versus concentration curves and the cmc values were found to depend on the range of points used in the cmc evaluation.

Introduction

In recent years, there has been increasing interest in the formation and the properties of block copolymer micelles.[1–4] These micelles are formed when the polymer concentration exceeds the critical micelle concentration (cmc), below which only single chains are present. The evaluation of this quantity can give considerable insight into the thermodynamics of micelle formation. Extensive data have been accumulated for micelles formed from low molecular weight surfactants,[5] but data for block copolymer micelles are still limited.

In the case of block copolymers, the cmc values are frequently lower than those in surfactants; in some polymer systems it is not even possible to observe the cmc under isothermal conditions. In some of these cases, the critical micelle temperature, cmt, has been evaluated.[3,6–10] The cmt as a function of solvent concentration in binary mixtures has also been studied.[11] A recent study bridges surfactants and polymers by investigating the cmc of monochelic polymers consisting of one ionic group attached to a polystyrene chain and reports the cmc under isothermal conditions.[12] The differences between the properties of monomeric and polymeric surfactants in both aqueous and nonaqueous solutions have also been studied.[13]

Micelle formation in block copolymers differs from that in surfactants because of differences in the formation process. Below the cmc, monomolecular micelles[1,14] are postulated to exist in block copolymers, where the soluble block surrounds the insoluble block copolymer, keeping the insoluble block in solution. The insoluble block in this unfavorable solvent is in a collapsed conformation and, as the polymer concentration increases, the insoluble blocks are attracted to each other and begin to associate. During this process, the solvent is progressively driven out of the micelle core, which would explain the swelling of the micelle near the cmc that has been observed on dilution in some systems.[15–18] Also, stopped flow experiments have found that the first step for the dissociation of triblock copolymer micelles is an influx of solvent molecules into the core.[19]

An important factor in the cmc properties of block copolymer micelles is the polydispersity of the polymer chains. A recent micellization model[20] accounts for this effect by using an extension of a mixed micelle model developed by Holland and Rubingh[21,22] for low molecular weight surfactants. It was found that the concentration of single chains increases as a function of total polymer concentration. This effect becomes more important as the polydispersity increases. Thus, a sharp cmc cannot be observed for block copolymer micelles formed from polydisperse blocks. Therefore, techniques which monitor micelles rather than the change in single chains are preferable for the cmc determination of block copolymer micelles.[20] Many such techniques have been used to determine the cmc, including fluorescence,[23–25] light scattering,[15,26–28] osmometry,[3,29] and viscosity.[29]

Static light scattering (SLS) is a technique sensitive to the weight-average molecular weight, M_w, of the species in solution. As a solution composed primarily of micelles is diluted, the solution composition changes to a system which contains comparable amounts of micelles and unimers. Upon further dilution, the cmc is reached and the solution contains only unimers. This transition can be followed from the behavior of the inverse molecular weight as a function of concentration. This quantity can be monitored, for example, from the ratio of the concentration to scattered intensity, as in the case of light scattering, or from the behavior of the reduced osmotic pressure, as in the case of osmometry. Several workers have found these trends, and the cmc was taken as the point below which the inverse molecular weight remained constant, i.e., where only unimers were present.[3,30–32] This point is shown schematically in Figure 1 in a plot of the

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reciprocal apparent weight-average molecular weight, $(M_w)_{app}^{-1}$, as a function of concentration. In this figure, $(M_w)_{app}^{-1}$ is depicted as $Kc/R(0)$ as in the case for SLS, where K is the optical constant, c is the concentration, and $R(0)$ is the Rayleigh ratio extrapolated to zero angle. Three regions are represented in this figure: (a) unimer region, (b) coexistence of unimers and micelles, and (c) predominantly micellar region. Some polymeric micelles have extremely low cmc values, and the unimer region cannot be observed by the above methods. In these cases, cmc determination is difficult, and the Debye equation[33] has been used as an approximation for the cmc evaluation.[34-36] Other extrapolations of the scattered intensity from the lower micelle region to the value for the unassociated polymer have also been employed to determine the cmc.[37]

This paper introduces a method of evaluating the cmc for systems where only the micelle region and a part of the transition region of micelles to unimers is observed in the absence of the single chain region. A method was designed to evaluate the cmc from static light scattering measurements using a recent micellization model for block copolymers in solution which takes the polydispersity of the block copolymer into consideration.[20] The increase of the inverse apparent molecular weight was analyzed as a function of decreasing concentration, but the present method does not address the anomalous micellization phenomena which have been observed in some systems.[29,38-41] The purpose of this paper is to illustrate the cmc determination by SLS using this method for reverse micelles formed by two block copolymer systems. The first is a block ionomer, poly(styrene-*b*-sodium acrylate) (PS-*b*-PANa), having a polystyrene block of a constant length attached a sodium acrylate block of varying length; the second is a nonionic block copolymer, poly(styrene-*b*-4-vinylpyridine) (PS-*b*-P4VP). An extensive study of these systems will be subject of a later paper.[42] The present paper consists of a brief description of the theory and of the method, followed by results for the two systems. The effect of the polydispersity on the cmc is shown by generating $Kc/R(0)$ versus concentration curves for the poly(styrene-*b*-isoprene) (PS-*b*-PI) system. The discussion addresses the results of the cmc determination as well as the effect of polydispersity.

Theory

Static light scattering is a convenient method for the characterization of micelles. When the particle size is not small compared to the wavelength of light, then the following relation applies:[43]

$$Kc/R(\theta) = \frac{1}{P(\theta)M_w} + 2A_2c + \dots \qquad (1)$$

where K is the optical constant $(2\pi^2(n\ \mathrm{d}n/\mathrm{d}c)^2/\lambda_0^4N_A)$, n is the refractive index, $\mathrm{d}n/\mathrm{d}c$ is the specific refractive index increment at a constant chemical potential, λ_0 is the wavelength in vacuum, N_A is Avogadro's number, c is the concentration, $R(\theta)$ is the Rayleigh ratio at the angle of measurement, $P(\theta)$ is the particle scattering function, and A_2 is the second virial coefficient; the higher order virial coefficients have been neglected, which is valid for sufficiently dilute solutions. The particle scattering function describes the angular variation of the intensity and takes into account the intraparticle interference. When the data are extrapolated to 0°, this term becomes equal to one. In the case of block copolymers, the weight-average molecular weight is an apparent one due to the chemical heterogeneity of the copolymer.[44,45]

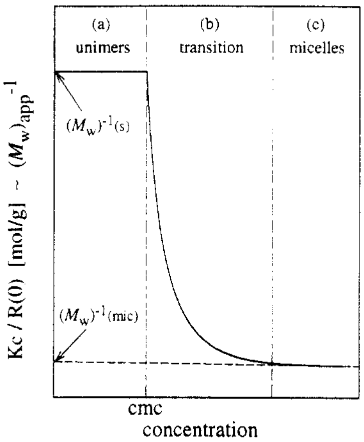

Figure 1. Range of existence of different species in solution as a function of concentration according to the closed association model.[33]

The micellization model developed recently for block copolymers[20] addresses some of the differences between the micellization of block copolymers and of surfactants by accounting for the polydispersity of the block copolymer and the dependence of the cmc on the length of the insoluble block. In the case of low molecular weight surfactants, the static light scattering data can be evaluated in terms of the Debye equation[33]

$$K(c - \mathrm{cmc})/(R(0) - R_{\mathrm{cmc}}) = 1/(M_N)_w + 2A_2(c - \mathrm{cmc}) + \dots \qquad (2)$$

where $R(0)$ is the Rayleigh ratio extrapolated to 0°, R_{cmc} is the Rayleigh ratio at the cmc, $(M_N)_w$ refers to the apparent weight-average molecular weight of the aggregate, and A_2 is the second virial coefficient; the higher order virial terms are neglected. This model can be applied only to micelles formed by monodisperse block copolymers.

For polydisperse block copolymers, the single chain concentration is not constant at different total polymer concentrations. In the case of a polydisperse system, eq 2 is modified by replacing the cmc with the total single chain concentration, S, and the apparent weight-average molecular weight is given in terms of the sum of the weighted fraction of the apparent weight-average molecular weight of the species in solution; i.e., $M_w = (\sum c_iM_i)/c$. This yields

$$Kc/R(0) = 1/[M_w(\mathrm{s}) \times S/c + M_w(\mathrm{mic}) \times (1 - S/c)] + 2A_2c \qquad (3)$$

where $M_w(\mathrm{s})$ and $M_w(\mathrm{mic})$ are the apparent weight-average molecular weights of the single chain and the micelle, respectively. Equation 3 is equivalent to eq 2 when the second virial coefficient is zero.

Theoretically the molecular weight distribution of living polymers is expected to be a Poisson distribution.[46] However, experimentally, distributions have been found to be broader, and the Gaussian distribution has been suggested as a reasonable representation of the system.[47] In this model, the polydispersity of the insoluble block, which has a greater effect on the cmc than that of the soluble block, is described by a Gaussian distribution, and the mole fraction of the ith component in the mixture, α_i, is given by

$$\alpha_i = (2\pi)^{-1/2}\sigma^{-1} \exp[-(N_i - N)^2/2\sigma^2] \qquad (4)$$

where $\sigma = \mathrm{DP_n}(\mathrm{PI} - 1)^{1/2}$, $\mathrm{PI} = \mathrm{DP_w}/\mathrm{DP_n}$, and $N = \mathrm{DP_n}$. Here PI, $\mathrm{DP_n}$, and $\mathrm{DP_w}$ refer to the polydispersity index, the number-average degree of polymerization, and the weight-average degree of polymerization, respectively.

It should be noted that for broader distributions, i.e., when the polydispersity index is high, the Gaussian distribution may no longer be applicable due to the truncation of the distribution function for chain lengths at zero. In these cases, other distribution functions such as the Schulz–Flory distribution[46] should be employed. The amount of truncation which occurs for the polydispersity indices used in the present case (1.1 and 1.2) is not significant. For example, for polydispersity indices of 1.1 and 1.2, more than 99.9% and 98.8% of the area under the curve, respectively, is used in the calculation for the mole fraction. The truncation would naturally be larger for higher polydispersity indices. The area which is covered in the Gaussian distribution can be evaluated for different polydispersity indices from the definition of σ, and for a range of 3σ, more than 99.7% of the area is used.

The mole fraction of the ith component in the micellar phase, x_i, is given as

$$x_i = (\alpha_i C)/(C + f_i C_i - S) \qquad (5)$$

where C is the total concentration of the mixture, f_i is the activity coefficient, which can be assumed to be unity for ideal mixing, C_i is the cmc for a monodisperse polymer, and S is the total single chain concentration.

This model predicts the dependence of the free energy of micellization on the length of the insoluble block for block copolymer micelles. It has been suggested[20] that the insoluble block collapses to form a ball when the polymer is in the single chain state. The free energy of interaction for the collapsed blocks can be accounted for by the Hamaker equation, in which the free energy is proportional to the sphere radius. Since the collapsed blocks interact only with those found in their proximity, the free energy of micellization is proportional to the radius of the collapsed insoluble block. Since the volume of the micellar core is proportional to N, the number of repeat units in the insoluble block, the radius of the sphere is related linearly to $N^{1/3}$. Thus, the cmc for a monodisperse polymer is given by

$$\log C_i = aN^{1/3} + b \qquad (6)$$

where a and b are constants. This equation is valid only for a collapsed block and differs from that for surfactants, where the cmc is found to be proportional to the number of methylene groups.[48–51] The cmc for a polydisperse system, cmc(mix), is evaluated from the following

$$\mathrm{cmc(mix)} = \{\sum_i^n (\alpha_i/f_i C_i)\}^{-1} \qquad (7)$$

In this paper, the theory described above is used to determine the cmc by fitting the light scattering data, $Kc/R(0)$, as a function of concentration. The a and b constants are determined from a minimization of χ, which is defined by the following equation:

$$\chi^2 = \sum [(Kc/R(0))_{\mathrm{expt}} - (Kc/R(0))_{\mathrm{cal}}]^2/(Kc/R(0)_{\mathrm{expt}})^2 \qquad (8)$$

where the calculated ratio of $Kc/R(0)$ is obtained using eq 3.

The parameters used for the calculation are the concentration (molar), $Kc/R(0)$ (mol/g), the number of repeat units in the insoluble block, the polydispersity of the insoluble block, which is assumed to be similar to that of the soluble block (1.10), and the apparent weight-average molecular weights of the micelles and single chains. Since the cmc value is very low, no correction is needed for the single chain content, and the micelle apparent molecular weight used is determined from a Zimm plot in the high-concentration region. For the block copolymer series, the data for each copolymer mentioned above are combined for the calculations. The calculations are performed first for a constant value of b and varying a, and when the iterations are complete for the range of a values, the b value is changed and the process is repeated. A common step size used in the final determination of the a and b values is 0.01. For each point on the Gaussian distribution, C_i is evaluated from eq 6, and eq 5 is summed. The total single chain concentration is varied and the process is repeated until the $\sum x_i$ is equal to unity or for a maximum of 15 000 iterations. This calculation is repeated for the required range of a and b values, and the minimum values as determined by eq 8 are obtained. The light scattering curves of $Kc/R(0)$ versus concentration can be generated for a given polymer once the a and b values have been determined.

Experimental Section

Sample Preparation. The block copolymers, poly(styrene-*b*-sodium acrylate) and poly(styrene-*b*-4-vinylpyridine), were prepared by sequential anionic polymerization; the details are given in refs 52 and 53, respectively. The polydispersity of the homopolystyrene block was determined from size exclusion chromatography (SEC) in tetrahydrofuran before the addition of the second block. For the light scattering measurements, the polymer samples were dried for 4 days at 60 °C in a vacuum oven. The PS-*b*-PANa and the PS-*b*-P4VP block copolymers were dissolved in dry tetrahydrofuran (distilled over a sodium benzophenone complex) and in dry toluene (distilled over calcium hydride), respectively. The solvent and polymer solutions were filtered through 0.2 and 0.45 μm PTFE filters, respectively, into scintillation vials which were used for the light scattering measurements. A minimum of four concentrations were used to determine the weight-average molecular weight, radius of gyration, and second virial coefficient by constructing a Zimm plot. The cmc measurement was performed by successive dilutions of the samples. The intensity values for each concentration were extrapolated to zero angle, and these values were used in the cmc determination.

Static Light Scattering. Light scattering experiments were performed using a Dawn-F multiangle laser photometer (Wyatt Technology, Santa Barbara, CA) equipped with a He–Ne laser (632.8 nm). Data acquisition and analysis utilized the DawnF and SkorF software, respectively. Zimm plots were processed with Aurora software. The specific refractive index increment was determined using the Wyatt/Optilab 903 interferometric refractometer and accompanying software (Dndc 2.01) at a 630 nm wavelength. Five to eight concentrations were measured for each specific refractive index increment determination.

Results and Discussion

PS-*b*-PANa System. A typical plot of $Kc/R(0)$ versus concentration for the fitted experimental points for one of the block ionomers, polystyrene(660)-*b*-poly(sodium acrylate)(8.9), is given in Figure 2. As previously discussed, the light scattering curve does not show the unimer region, which could not be attained by this method because the value of the scattered intensity was far too low to be determined by the light scattering measurement. The $Kc/R(0)$ value for the unimer region was estimated from the weight-average molecular weight of the homopolystyrene with 660 units and was found to be approximately 13×10^{-6} mol/g, thus making the extrapolation of the present

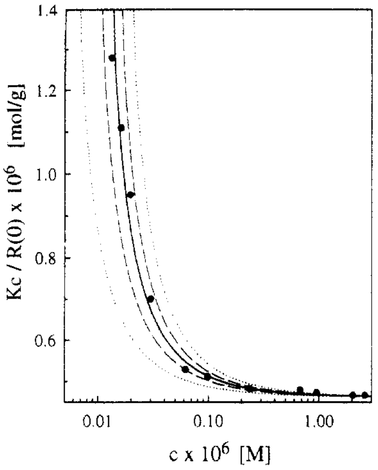

Figure 2. Typical cmc determination for PS(660)-*b*-PANa(8.9) in THF from the program calculations (—) and with intentional deviations of 20% (- - -) and 50% (···).

Table 1. Critical Micelle Concentration for the Poly(styrene-*b*-sodium acrylate) Series in THF

	cmc (M)		
PS(*X*)-*b*-PANa(*Y*)	polydisperse (eq 7)	Debye eq (eq 2)	% diff
660-*b*-2.6	2.5×10^{-8}	2.1×10^{-8}	16
660-*b*-4.7	1.6×10^{-8}	1.3×10^{-8}	19
660-*b*-6.4	1.2×10^{-8}	1.5×10^{-8}	25
660-*b*-8.9	9.0×10^{-9}	9.2×10^{-9}	2.2
660-*b*-14	5.4×10^{-9}	5.0×10^{-9}	7.4

curve unfeasible. However, the micelle region and the beginning of the transition region of the micelles to the unimers was observed and used in the cmc determination by the program. The *a* and *b* values, evaluated according to the calculation program, were found to be −0.64 and −6.71, respectively. Once these constants are known, the relation between the cmc of the monodisperse block copolymer and the insoluble block length as well as the effect of polydispersity can be evaluated.

Theoretical $Kc/R(0)$ values were generated for different cmc values to determine the sensitivity of the calculated cmc value. This was accomplished by varying either the *a* or the *b* constant determined in the fitting procedure. The percent deviation from the determined cmc value (9.2×10^{-9} M) and the corresponding cmc value were ±20% (1.1×10^{-8} and 7.4×10^{-9} M) and ±50% (1.4×10^{-8} and 4.6×10^{-9} M). These curves are plotted in Figure 2 as a solid line for the cmc value, dashed lines for the 20% difference, and dotted lines for the 50% difference. The sensitivity of the cmc determination for this method falls approximately within the 20% limit. It is also interesting to note that a 20% and a 50% error in the cmc value corresponds approximately to a 1% and 5% error in the *b* value and similarly an 8% and 20% error in the *a* value, respectively. The *a* and *b* values must therefore be evaluated precisely.

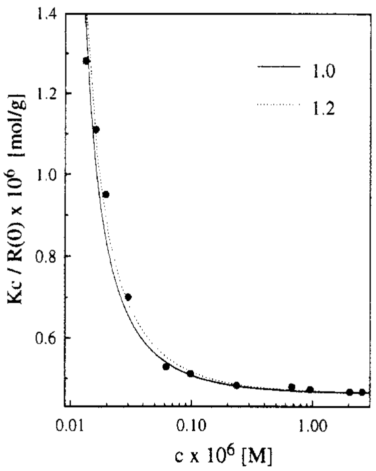

Figure 3. Effect of the polydispersity index on the cmc determination of PS(660)-*b*-PANa(8.9) in THF.

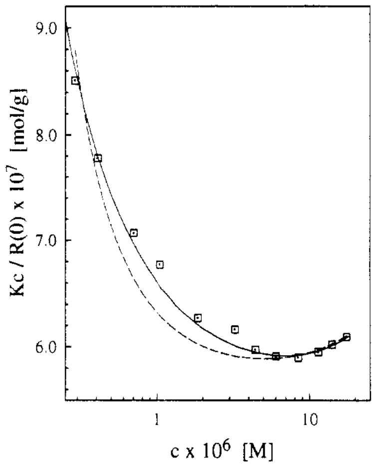

Figure 4. Cmc determination for PS(470)-*b*-P4VP(52) in toluene; the lines (—) and (- - -) represent the fits obtained from the current method and the Debye equation, respectively.

The cmc values determined by using a curve fitting program involving the Debye equation (eq 2) for the cmc were found to be within experimental error of the values using the present program (Table 1). This result is not surprising since the polydispersity of the block was estimated to be less than 1.1.[47] Also, the low magnitude of the *a* constant (−0.64) in eq 6 shows that there is a relatively weak dependence of the cmc on the length of the insoluble block; furthermore, the insoluble block length is relatively short. The polydispersity should therefore not have a great effect on the fit of the Debye equation. To see the effect of the polydispersity, $Kc/R(0)$ values as a function of concentration were calculated assuming different polydispersity indices. These values are represented by lines in Figure 3, where the symbols represent the measured data. The cmc values from the different polydispersity indices of 1.0, 1.1, and 1.2 were 9.2×10^{-9}, 9.0×10^{-9}, and 8.7×10^{-9} M, respectively. The percent deviation for the polydispersity indices of 1.1 and 1.2 from the 1.0 value were 2% and 5%, respectively. These values indicate that in the present system the effect of polydispersity on the cmc values is not very large as could be predicted from the small value of the *a* constant.

PS-*b*-P4VP System. The cmc of the second system, polystyrene(470)-*b*-poly(4-vinylpyridine)(52), was measured in toluene, and the data are shown in Figure 4. The *a* and *b* constants determined using the current method were −1.66 and −0.90, respectively. The solid and dashed lines represent the fit of the experimental data obtained from the program and from the Debye equation, respectively. The current method is able to describe the points in the transition region very well in contrast to the Debye equation. The cmc values determined from these two methods differ by a factor of ca. 3; the cmc values were 3.5×10^{-8} and 1.1×10^{-7} M, as obtained by the current method and by the Debye equation, respectively. For this system, the Debye equation does not describe the light scattering curves and the cmc value. This result is due to the greater dependence of the cmc value on the length of the insoluble block, as determined by the value of the *a* constant; also the length of the insoluble block was greater as compared to that of the PS-*b*-PANa block ionomer series.

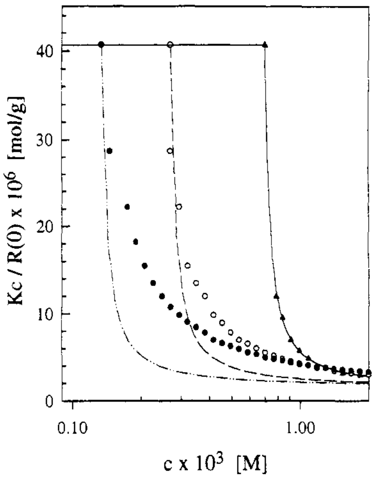

Figure 5. Effect of polydispersity index on the cmc values for simulation data of a PS-*b*-PI system. The symbols represent the data generated for different polydispersities: (▲) 1.0; (○) 1.1; and (●) 1.2. The lines represent the fit from the Debye equation through the simulated data for the different polydispersity indices: (—) 1.0; (- - -) 1.1; (- ••) 1.2.

PS-*b*-PI System. To illustrate the effect of the polydispersity on the cmc values, the polystyrene-*b*-polyisoprene system was modeled by assuming different polydispersity indices for the insoluble block. The *a* and *b* constants for this system in *n*-hexadecane, from the results of Price et al.,[6] were previously determined to be −1.65 and 3.55, respectively.[20] The higher magnitude of the *a* constant shows a stronger dependence of the cmc values on the insoluble block length as compared to the block ionomer system. The $Kc/R(0)$ values as a function of concentration were calculated as described previously for different polydispersity indices. The parameters used for the generation of these values were the *a* and *b* constants, an insoluble block length of 67, a second virial coefficient value of zero, and a single chain and micellar apparent weight-average molecular weight of 2.4×10^4 and 5.4×10^5, respectively. The results are represented by symbols in Figure 5 for the polydispersity indices of 1.0, 1.1, and 1.2, respectively. It can be seen from these points that there is a large effect of the polydispersity index on the cmc values. For instance, the cmc value for a polydispersity index of 1.0 (7.0×10^{-4} M) decreases approximately 2.6 times and 5.4 times for a polydispersity index of 1.1 (2.7×10^{-4} M) and 1.2 (1.3×10^{-4} M), respectively.

The applicability of the Debye equation to this system at various polydispersities was investigated by fitting the generated points according to eq 2. For the polydispersity index of 1.0, the Debye equation fits the generated points very well. However, for the higher polydispersity indices, the Debye equation clearly cannot account for the behavior of the $Kc/R(0)$ values as a function of concentration. However, the cmc values for the higher polydispersity indices agree with the real cmc values even though the fit does not pass through all or even most of the points in the transition region. It should be noted that these cmc values were determined from the generated points, including the first point of the unimer region.

In general, for low cmc values the unimer region may not be attainable. Therefore, it is of interest to compare the results of the fit when the highest value of the inverse apparent molecular weight is less than that at the unimer line. In this case, the cmc values as obtained from eq 2 deviate progressively from the real cmc value as the polydispersity increases. For instance, when the $Kc/R(0)$ value or the inverse $(M_w)_{app}$ is 3 times less than the inverse unimer molecular weight, the cmc values for the polydispersity indices of 1.1 and 1.2 were 3.8×10^{-4} M (41%) and 2.3×10^{-4} M (77%), respectively, where the number in parentheses denotes the percent error from the generated cmc value.

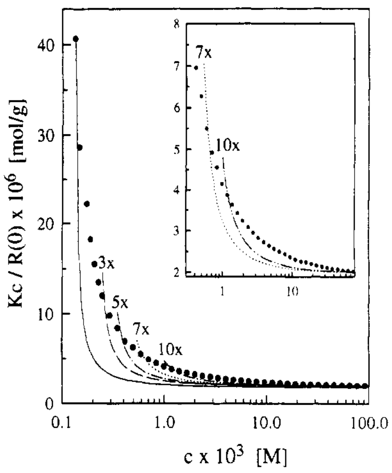

Figure 6. Debye equation fit for the stimulated data of the PS-*b*-PI system with a polydispersity index of 1.2. The solid line indicates the fit when the first point on the unimer line is included. The other lines represent the fits for different ranges of $Kc/R(0)$ values used. These ranges are indicated by numbers which refer to the ratio of the $Kc/R(0)$ value for the unimer to the cutoff value. The inset graph is a magnification of the 7 and 10 times ratio, respectively.

The cmc values as evaluated by the Debye equation were found to depend on the range of data values used in the fit. Figure 6 illustrates this effect for the polydispersity index of 1.2. For example, when the inverse $(M_w)_{app}$ is ca. 5, 7, or 10 times lower than that in the unimer region, the corresponding cmc values as evaluated from the Debye equation were 3.0×10^{-4} (2.3), 4.2×10^{-4} (3.2), and 6.1×10^{-4} (4.7), respectively, where the numbers in parentheses denote the ratio of the cmc value to the real cmc value. Figure 6 also illustrates that when the range used in 7 and 10 times lower than the unimer line, the points still show the transition region of micelles to unimers. Thus for polydisperse block copolymer systems which have significant dependence on the cmc on the insoluble block length, the Debye equation is no longer applicable and the cmc values must be accounted for by the present approach.

Conclusions

The present method, which uses a fitting procedure based on a micellization model for block copolymers in solution, was able to evaluate the cmc for block copolymer micelles from SLS data, for cases where scattering from the unimer region was not measurable. Certain characteristic features of the micellization of block copolymers, such as the change of the total single chain concentration with the total polymer concentration and the polydispersity of the insoluble chain, were accounted for by this method. The values of the *a* and *b* constants, which describe the dependence of the log(cmc) on $N^{1/3}$, were evaluated. These values are constant for a series of block copolymers consisting of a constant block length for the soluble block and different lengths for the insoluble block. These constants allow the prediction of the cmc values for different insoluble block lengths as well as of the effect of the polydispersity index of the insoluble block on the cmc values. It was found that the cmc values as evaluated from this program are accurate within approximately 20%.

The effect of the polydispersity on the cmc depends on the size of the *a* constant, which characterizes the insoluble block length dependence. For the block ionomer series, it was found that this dependence was weak and the cmc values generated by assuming different polydispersity indices did not change significantly. In the case of the PS-*b*-P4VP system, the dependence of the cmc on the insoluble block length was stronger, and the cmc could only be evaluated by the present approach. The PS-*b*-PI system was modeled to show the effects of the polydispersity on a system which has a significant dependence of the cmc on the insoluble block length. It was found that the Debye equation was able to evaluate the cmc values only when the first point of the unimer line was used in the determination, even though the fit did not pass through the data points in the transition region. However, the unimer region is often impossible to measure, and for these cases the Debye equation is not able to describe the cmc values. In general, for block copolymer systems which have a low value of a, as well as monodisperse block copolymers, the Debye equation and the present approach are both able to represent the cmc values. However, for systems with higher a values and larger polydispersities, only the present approach is able to evaluate the cmc values.

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