

Characterization of pH-dependent micellization of polystyrene-based cationic block copolymers prepared by reversible addition-fragmentation chain transfer (RAFT) radical polymerization

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Abstract

A series of block copolymers composed of a fixed length of an (*ar*-vinylbenzyl)trimethylammonium chloride (**Q**) block (the number average degree of polymerization of the **Q** block, $DP_{n,Q}=57$) and varying lengths of an *N,N*-dimethylvinylbenzylamine (**A**) block (the number average degrees of polymerization of the **A** blocks, $DP_{n,A}$, ranging 11–50) were prepared by reversible addition-fragmentation chain transfer (RAFT) radical polymerization, and their pH-dependent micellization was characterized by potentiometric titration, ¹H NMR spectroscopy, dynamic and static light scattering, and fluorescence techniques as a function of the **A** block length. At pH < 5.5, the **A** block is fully protonated, and hence the block copolymers act as a simple polyelectrolyte, dissolving molecularly in acidic water. At pH > 7, the **A** block becomes deprotonated, and thereby the block copolymers aggregate into a micelle composed of hydrophobic microdomains formed from the deprotonated **A** blocks. Results of light scattering and fluorescence measurements indicated that the micellization behavior depended strongly on the length of the **A** block. The number of polymer chains comprising one micelle (i.e. mean aggregation number, N_{agg}) increased from 3 to 12 as $DP_{n,A}$ increased from 11 to 50 at pH 10.0. In the case of a random copolymer of **Q** and **A** with an **A/Q** molar ratio similar to that of a block copolymer with $DP_{n,A}=50$, $N_{agg} \sim 1$ (i.e. unimolecular micelle) was confirmed by static light scattering at pH 10.0.

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1. Introduction

Stimuli-responsive water-soluble polymers have been the subject of increasing interest because they may find a variety of practical applications, including personal care items, pharmaceuticals, paints, and coatings [1]. Recent developments in controlled polymerization [2] have allowed synthesis of various types of stimuli-responsive water-soluble polymers

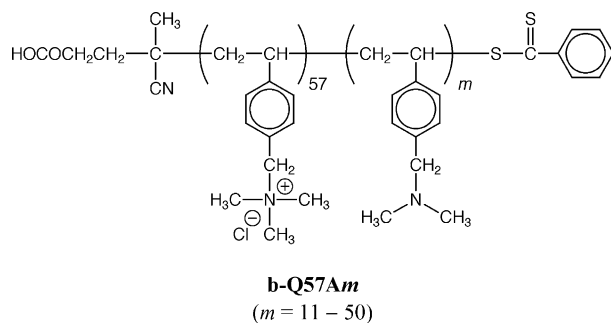
with well-designed chemical structures [3], and thus interesting stimuli-responsive properties, such as micellization and sol–gel transitions, have been reported [4].

Recently, McCormick et al. [5] have reported the successful synthesis of pH-responsive polystyrene-based block copolymers, including a cationic block copolymer of (*ar*-vinylbenzyl)trimethylammonium chloride (**Q**) and *N,N*-dimethylvinylbenzylamine (**A**), by reversible addition-fragmentation chain transfer (RAFT) radical polymerization in aqueous media. Well-defined, stimuli-responsive polycations have been a rather under-examined subject of investigation [6–10], although they are potential candidates for nano-sized vehicles in drug delivery systems [11–13]. Furthermore, homo- and copolymers of **Q** may provide a promising material for applications such as antibacterial agent [14] and paper sizing agent [15].

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Scheme 1. Structure of the block copolymers (**b-Q57Am**).

In this study, we prepared a series of block copolymers of **Q** and **A** monomers composed of a fixed **Q** block length and differing **A** block lengths (Scheme 1) by RAFT [5] and characterized their pH-dependent self-assembly as a function of the length of the **A** block. The micellization behavior of one of the block copolymers was compared with that of a random copolymer whose **A/Q** molar ratio and molecular weight are similar to those of the block copolymer.

2. Experimental

2.1. Materials and polymers

(*ar*-Vinylbenzyl)trimethylammonium chloride (**Q**) and *N,N*-dimethylvinylbenzylamine (**A**) were purchased from Aldrich Chemical Company. **Q** was used as received and **A** was purified by distillation under reduced pressure. 4,4'-Azobis(4-cyanopentanoic acid) (V-501) was a gift from Wako Pure Chemical Industries and purified by recrystallization from methanol. *N*-Phenyl-1-naphthylamine (PNA) was purchased from Wako Pure Chemical Industries and purified by recrystallization from methanol. Water was purified with a Millipore Milli-Q system.

Block copolymers were prepared from **Q** and **A** monomers using V-501 and 4-cyanopentanoic acid dithiobenzoate (CPADTB) as initiator and chain transfer agent (CTA), respectively, as reported elsewhere [5]. A random copolymer of **Q** and **A** was prepared as follows: **Q** (2.27 g, 10.7 mmol), **A** (1.73 g, 10.7 mmol), V-501 (9.8 mg, 35 μ mol), and CPADTB (55.9 mg, 0.20 mmol) were dissolved in water (20 mL). Hydrochloric acid (6.0 M) was added to the solution to solubilize the **A** monomer. The final solution pH was adjusted to 7.0. The solution was deoxygenated by purging with Ar for 30 min, and then warmed at 70 °C with an oil bath for 24 h. The copolymers obtained were purified by dialysis against pure water for a week and recovered by lyophilization.

2.2. Measurements

Gel-permeation chromatography (GPC) analysis was performed on a JASCO GPC-900 instrument equipped with a JASCO RI-930 refractive index detector using a Shodex OHPak SB-804 HQ column at 40 °C at a flow rate of 1.0 mL/min. A 0.30 M Na₂SO₄ aqueous solution containing

0.50 M acetic acid was used as eluent. Values of M_n and M_w/M_n for the polymers were estimated as follows: For each polymer sample, M_w was measured by static light scattering (SLS) (see below), and the M_w value was plotted against the GPC peak elution volume to obtain a calibration curve. Using the calibration curve, M_n was estimated from GPC elution data. The number average degree of polymerization of the **Q** block ($DP_{n,Q}$) was calculated from M_n for the macro-CTA (**Q57**) to be 57. The number average degrees of polymerization of the **A** blocks ($DP_{n,A}$) for the block copolymers were calculated from M_n values thus estimated for the block copolymers taking into account M_n for **Q57**.

Potentiometric titrations were carried out using a 10 mL of a 1.0 g/L aqueous solution of the copolymer. To this polymer solution, 20 μ L of 1.0 M HCl was added prior to titration to ensure that all the tertiary amine units were fully protonated. The sample solution was titrated with a 0.10 M NaOH aqueous solution using a microburet under an N₂ flow at 25 °C. During the titration, pH was monitored with a Horiba F-23 pH meter equipped with a Horiba 6366-10D glass electrode. The plot of pH versus the volume of the titrant (0.10 M NaOH) exhibited two distinctive inflections corresponding to the neutralization of excess HCl and the end point of the deprotonation (data not shown) [16]. The degree of protonation (α) was calculated from the volume of the titrant.

¹H NMR spectra were obtained with a Bruker DRX-500 spectrometer operating at 500 MHz. Chemical shifts were determined by using 3-(trimethylsilyl)propionic-2,2,3,3-*d*₄ acid as internal reference. For ¹H NMR measurements, sample solutions of the copolymers in D₂O containing 0.10 M NaCl were prepared at a polymer concentration (C_p) of 10.0 g/L, and pD was adjusted with a D₂O solution of NaOD or DCl. The final pH value was determined from the relation pH = pD - 0.4 [17].

Dynamic light scattering (DLS) data were obtained at 25 °C with an Otsuka Electronics Photol DLS-7000DL light scattering spectrometer equipped with an ALV-5000E multi- τ -digital time correlator. An Ar⁺ laser (30.0 mW at 488 nm) was used as a light source. Sample solutions ($C_p = 2.0$ g/L) for DLS measurements were filtered with a 0.2 μ m pore size membrane filter. To obtain the relaxation time distribution, $\tau A(\tau)$, the inverse Laplace transform analysis was performed using the algorithm REPES [18].

$$g^{(1)}(t) = \int \tau A(\tau) \exp\left(-\frac{t}{\tau}\right) d \ln \tau \quad (1)$$

Here, τ is the relaxation time and $g^{(1)}(t)$ is the normalized autocorrelation function. The average translational diffusion coefficient (D) was calculated from $D = \Gamma/q^2$, where Γ is the inverse of τ , i.e. the average relaxation rate, and $q = (4\pi n/\lambda) \sin(\theta/2)$ with n being the refractive index of solvent, λ being the wavelength (= 488 nm), and θ being the scattering angle. The intensity-average hydrodynamic radius (R_h) was calculated using the Einstein–Stokes relation, $R_h = k_B T / 6\pi\eta D$, where k_B is Boltzmann's constant, T is the absolute temperature, and η is the solvent viscosity.

SLS measurements were performed at 25 °C with an Otsuka Electronics Photal DLS-7000DL light scattering spectrometer equipped with an Ar⁺ laser (50 mW at 488 nm). Sample solutions for SLS measurements were filtered with a 0.2 μm pore size membrane filter. Values of M_w were estimated from the relation [19]

$$\frac{KC_p}{R_\theta} = \frac{1}{M_w} \left(+1 \frac{1}{3} \langle R_g \rangle^2 q^2 + \dots \right) + 2A_2 C_p + \dots \quad (2)$$

where R_θ is the Rayleigh ratio, R_g is the z -average radius of gyration, A_2 is the second virial coefficient, and $K = 4\pi^2 n^2 (dn/dc_p) / N_A \lambda^4$ with dn/dc_p being the refractive index increment against C_p and N_A being Avogadro's number. By measuring R_θ for a set of C_p and θ , M_w values were estimated from Zimm plots. Toluene was used for the calibration of the instrument. Values of dn/dc_p were determined with an Otsuka Electronics Photal DRM-1020 differential refractometer.

Fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. An aqueous stock solution of PNA (5.0×10^6 M) was prepared by adding 0.50 mL of a 5.0 mM PNA solution in methanol to 500 mL of a 0.10 M NaCl aqueous solution. A stock aqueous solution of the polymer ($C_p = 10.0$ g/L) was prepared as follows: a fully protonated polymer sample was first dissolved in the PNA stock solution such that the polymer concentration was slightly higher than 10.0 g/L. The pH value of the solution was adjusted to 10.0 by adding a 0.01 or 0.10 M NaOH solution prepared by dissolving NaOH in the PNA stock solution. Finally, the polymer concentration was adjusted to 10.0 g/L by adding a small amount of the PNA stock solution whose pH had been adjusted to 10.0. The polymer solution thus prepared was diluted to varying polymer concentrations and the sample solutions were allowed to stand for several hours for equilibration. For PNA fluorescence measurements, the sample solution was excited at 356 nm with excitation and emission slit widths being fixed at 5 nm.

3. Results and discussion

3.1. Molecular characteristics of the block copolymers

Listed in Table 1 are some molecular characteristics, including M_w , M_w/M_n , $DP_{n,Q}$, and $DP_{n,A}$ for all the block copolymers prepared in this study. The block copolymers are of an AB diblock type composed of a **Q** block of $DP_{n,Q} = 57$ and an **A** block of different $DP_{n,A}$ ranging 11–50. For the synthesis of the block copolymers (**b-Q57Am**, where m is $DP_{n,A}$), a homopolymer of **Q** with $DP_{n,Q} = 57$ (**Q57**) was used as a macro-CTA. Values of M_w/M_n for the block copolymers were relatively low, and were in the range 1.2–1.3, increasing slightly with an increase in the length of the **A** block. A random copolymer (**r-Q55A57**) of **Q** and **A** prepared for comparison with **b-Q57A50** in their associative behavior is also listed in Table 1. These two polymers are similar in molecular weight and in **A/Q** molar ratio but different in sequence distribution, i.e. random versus block sequences. Being a quaternary

Table 1
Molecular characteristics of the polymers

Polymer code	$M_w \times 10^{-4a}$	M_w/M_n^b	$DP_{n,Q}^c$	$DP_{n,A}^d$	A/Q ^e
Q57 ^f	1.2	1.2	57	0	0
b-Q57A11	1.8	1.2	57	11	0.19
b-Q57A22	2.1	1.3	57	22	0.39
b-Q57A34	2.3	1.3	57	34	0.59
b-Q57A50	3.2	1.3	57	50	0.87
r-Q55A57	3.2	1.2			1.04

^a Determined by SLS at pH 2.0 in 0.10 M NaCl.

^b Determined by GPC using a calibration curve of M_w against the peak elution volume for the copolymer samples, where M_w values were determined by SLS.

^c The number-average degree of polymerization for the **Q** block calculated from M_n determined by GPC.

^d The number-average degree of polymerization for the **A** block calculated from M_n determined by GPC.

^e Molar ratio of the **A** and **Q** units in copolymer.

^f Homopolymer of **Q** used as macro-CTA for the synthesis of the block copolymers.

ammonium group, the **Q** units in all the copolymers are cationic over the whole range of pH, whereas being a tertiary amine group, the **A** units are cationic under acidic pH and nonionic at neutral and basic pH.

Fig. 1(a) compares potentiometric titration data for a block (**b-Q57A50**) and random copolymer (**r-Q55A57**). Aqueous solutions of fully protonated polymers were titrated with a 0.10 M NaOH aqueous solution. At $pH < 5.5$, both the block and random copolymers are fully protonated. The deprotonation takes place progressively in a wide pH range of 5.8–8.8 for both the block and random copolymers but there is a clear difference between the two polymers in their deprotonation behavior in the pH range 6.2–7.5. As pH is increased in this pH range, the value of α for the block copolymer decreases more significantly than that for the random copolymer. At pH 7, for example, α values are about 0.5 and 0.7 for the block and random copolymers, respectively. This means that the block copolymer is more easily deprotonated than the random copolymer. Apparent pK_a values (the pH values at which $\alpha = 0.5$) for **b-Q57A50** and **r-Q55A57** can be estimated to be 7.1 and 7.3, respectively. Thus, the protonated block copolymer behaves as a stronger acid than does the protonated random copolymer. Such behavior has been reported for copolymers of 2-dimethylaminoethyl methacrylate and 2-methacryloyloxyethyltrimethylammonium iodide [20]. These observations suggest that the protonated **A** units are more densely confined to a limited space in the block copolymer than in the random copolymer. As can be seen in Fig. 1(b), where apparent pK_a is plotted against the length of the **A** block for **b-Q57Am**, pK_a for the block copolymer with $DP_{n,A} = 11$ is ca. 7.3, which is similar to that of **r-Q55A57**. As the length of the **A** block increases to 22, pK_a decreases to ca. 7.1, but the decrease in pK_a becomes much less pronounced as $DP_{n,A}$ further increases. These findings are an indication that partially protonated **A** blocks aggregate to form a microdomain where the **A** blocks are brought into a close proximity.

3.2. ^1H NMR

Fig. 2(a) shows ^1H NMR spectra for **b-Q57A50** measured at $C_p = 10.0$ g/L in D_2O containing 0.10 M NaCl at different pH values. At pH 2.0 (i.e. pD 2.4), **b-Q57A50** chains are fully protonated and hence solvated, and all the resonance bands expected for each block were clearly observed. Resonance bands in the $\delta = 1\text{--}2$ ppm region are attributed to methylene and methine protons in the polymer main chain. Resonance bands around $\delta = 2.5$ and 2.8 ppm are ascribable to methyl protons in the **A** and **Q** units, respectively. There are resonance bands due to benzylic protons in the **A** and **Q** units around $\delta = 4.1$ and 4.3 ppm, respectively. Resonance bands observed in the $\delta = 6.2\text{--}7.3$ ppm region are assignable to phenyl protons in the **A** and **Q** units. Under these conditions, **b-Q57A50** is molecularly dissolved in water (i.e. in a unimeric state). In the spectra measured at pH 8.5 and 10.0 (i.e. pD 8.9 and 10.4, respectively), resonance bands due to methyl and benzylic protons in the **A** units disappear completely, indicative of poor solvation and reduced mobility of the **A** block. From the chemical structure, it may be reasonable to expect that **b-Q57A50** will undergo supramolecular self-assembly forming a core-corona type polymer micelle with deprotonated **A** blocks forming the desolvated, hydrophobic core and permanently charged **Q** blocks forming the hydrophilic, solvated corona.

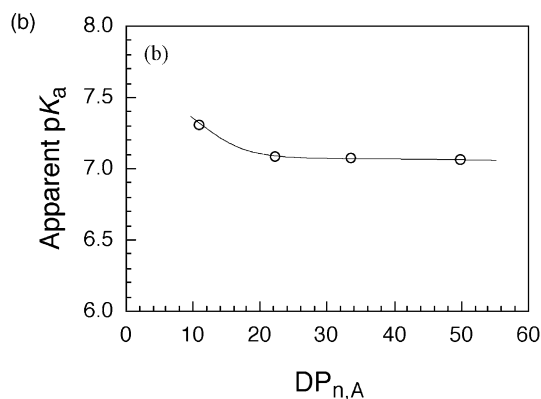
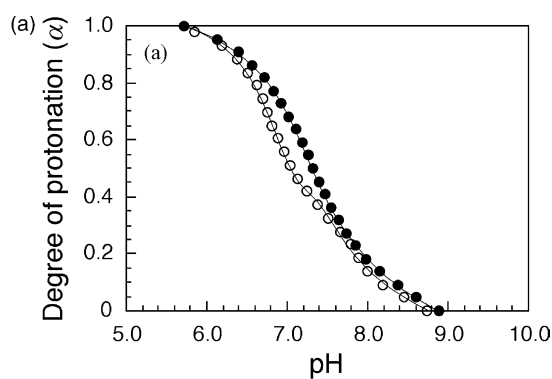


Fig. 1. Potentiometric titration curves for **b-Q57A50** (open circle) and **r-Q55A57** (solid circle) (a) and apparent pK_a plotted as a function of the length of the **A** block (b) Aqueous solutions of fully protonated polymers were titrated with a 0.10 M NaOH aqueous solution.

For comparison, Fig. 2(b) shows an example of ^1H NMR spectra for the random copolymer, **r-Q55A57**, measured at $C_p = 10.0$ g/L in D_2O containing 0.10 M NaCl at different pH values. At pH 2.0 (i.e. pD 2.4), the spectrum for **r-Q55A57** is almost the same as that for **b-Q57A50** (Fig. 2(a)), indicating that **r-Q55A57** chains are fully protonated and hence solvated. As pH is increased up to 10.0 (i.e. pD 10.4), resonance bands due to methyl and benzylic protons in the **A** units shift to higher magnetic fields, exhibiting a slight broadening. These spectra indicate that the random copolymer exhibits relatively high mobility, suggesting that the random copolymer forms a loosely associated micelle-like structure.

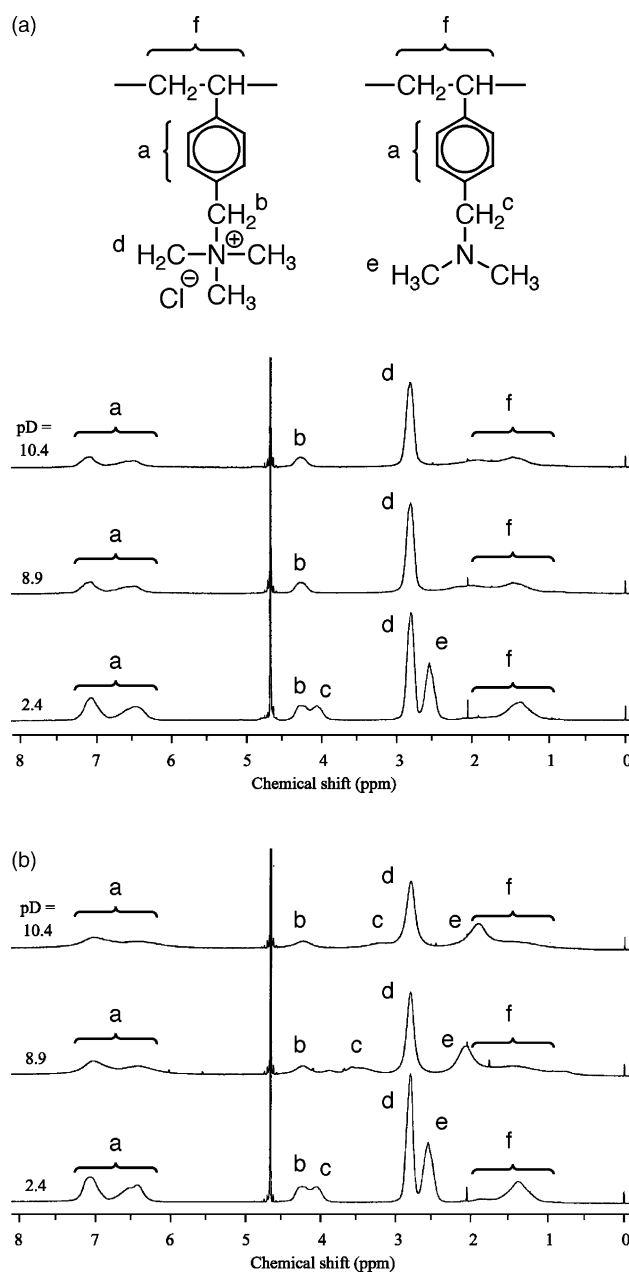


Fig. 2. ^1H NMR spectra for **b-Q57A50** (a) and **r-Q55A57** (b) in D_2O containing 0.10 M NaCl at varying pD.

3.3. Light scattering

Fig. 3 compares relaxation time distributions for **b-Q57A50** and **r-Q55A57** at pH 2.0 and 10.0 in 0.10 M NaCl. The relaxation time distributions for the block and random copolymers are unimodal at pH 2.0 and 10.0. Plots of the inverse of average relaxation time (I) against the square of the magnitude of the scattering vector (q^2) for **b-Q57A50** and **r-Q55A57** at pH 2.0 and 10.0 were confirmed to be linear passing through the origin (data not shown). Therefore, the relaxation mode is virtually diffusive. Approximate values of R_h were calculated from the Stokes–Einstein relation along with the viscosity of water using approximate values of the diffusion coefficients estimated from the slopes of the $I-q^2$ plots. In the case of **b-Q57A50** (Fig. 3(a)), the relaxation mode at pH 2.0 is attributed to a unimer with $R_h=3.3$ nm whereas the slow relaxation mode at pH 10.0 to a polymer aggregate with $R_h=8.9$ nm. It should be reasonable to consider that the polymer aggregate is a micelle with **A** blocks forming a core and **Q** blocks forming a corona. In the case of **r-Q55A57** (Fig. 3(b)), R_h values at pH 2.0 and 10.0 are estimated to be 3.5 and 2.8 nm, respectively, the hydrodynamic size being slightly larger at pH 2.0 than at pH 10.0.

Fig. 4(a) shows estimated R_h values for all the block copolymers plotted as a function of pH. At pH < 7, the block copolymers with longer **A** blocks show slightly larger R_h values. The R_h values for each block copolymer are essentially constant at pH < 7. These data indicate that all the block copolymers exist in the unimeric state at pH < 7. There appears to be a pH at which self-assembly starts to occur. As pH is

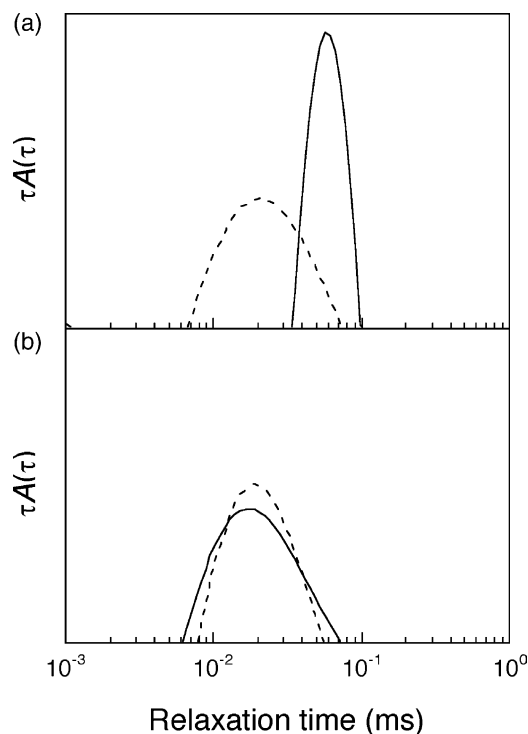


Fig. 3. DLS relaxation time distributions for **b-Q57A50** (a) and **r-Q55A57** (b) at pH 2.0 (broken line) and 10.0 (solid line). The polymer concentration was fixed at 2.0 g/L.

increased, R_h values for all the block copolymers abruptly increases near pH 7—the pH at which ca. 50% of the **A** units are still protonated. This increase in the hydrodynamic size is indicative of the formation of a micelle under basic conditions. When the partially protonated **A** blocks associate to form a domain, further deprotonation would occur more easily because of an electrostatic effect, and therefore, once the association starts to occur, additional associations can occur more easily. Thus, the micellization proceeds cooperatively. At pH > 7, the hydrodynamic size increases with increasing pH, and R_h values seem to level off at pH ≥ 10.

For comparison, R_h values for the random copolymer are also plotted as a function of pH in Fig. 4(a). In contrast to the block copolymers, the R_h value is much less dependent on pH, showing a slight decrease at pH > 7. At pH < 7, the hydrodynamic size for **r-Q55A57** is similar to that of **b-Q57A50**. That is to say, at pH 2.0, R_h values for the random copolymer and the block copolymer are 3.5 and 3.3 nm, respectively. At pH 10.0, however, the R_h value for **b-Q57A50** increases to 8.9 nm whereas that for **r-Q55A57** decreases to 2.8 nm. This observation suggests that the random copolymer undergoes intramolecular hydrophobic association whereas the block copolymer undergoes multipolymeric association [21,22].

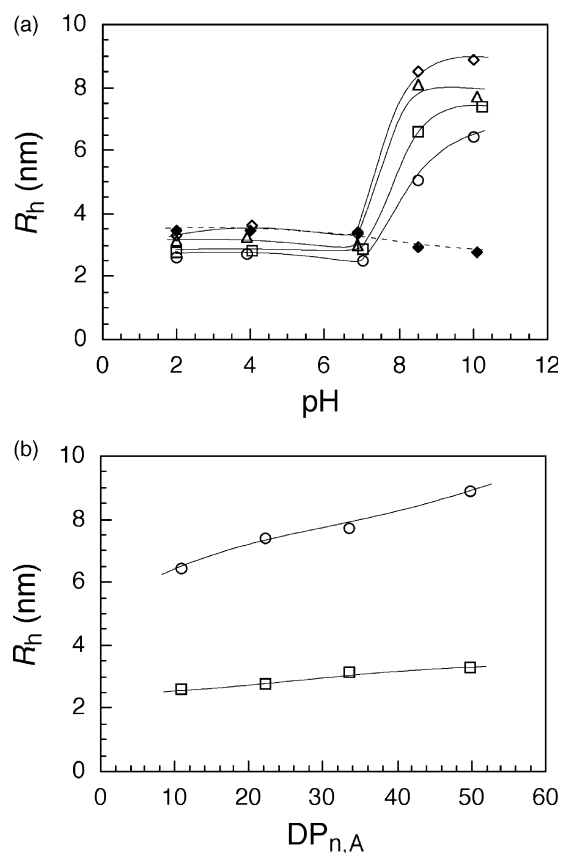


Fig. 4. Hydrodynamic radius plotted as a function of pH for **b-Q57A11** (open circle), **b-Q57A22** (open square), **b-Q57A34** (open triangle), **b-Q57A50** (open diamond), and **r-Q55A57** (solid diamond) (a) and hydrodynamic radius plotted as a function of the length of the **A** block at pH 2.0 (square) and 10.0 (circle). The polymer concentration was fixed at 2.0 g/L.

In Fig. 4(b), R_h values at pH 2.0 and 10.0 are plotted as a function of the length of the A block. At pH 2.0, all the block copolymers dissolve molecularly in 0.10 M aqueous NaCl with a coil conformation behaving as a simple polyelectrolyte, and hence the increase in the hydrodynamic size with increasing $DP_{n,A}$ simply reflects the increase in the polymer coil size with increasing molecular weight of the polymer. The observed values of R_h at pH 10.0 are those for polymer micelles formed from the block copolymers. The micelle size increases gradually with increasing length of the A block up to $DP_{n,A} = 50$.

Molar masses of all the block copolymers in the unimeric and micellar states were measured by SLS under acidic and basic conditions, respectively. Zimm plots for **b-Q57A50** obtained in 0.10 M NaCl at pH 2.0 and 10.0 are shown in Fig. 5(a) and (b), respectively. The values of M_w for the unimer and micelle of **b-Q57A50** were determined to be 3.2×10^4 and 3.5×10^5 , respectively, by extrapolation of C_p and θ to zero in the Zimm plots. By dividing the M_w value for the micelle by that for the unimer, the aggregation number (N_{agg}), i.e. the number of polymer chains consisting of one micelle, can be estimated to be ca. 12. It is to be noted that R_g values for the unimer and micelle are too small to be determined from the Zimm plots. In Fig. 6, values of N_{agg} estimated for all the block copolymers are plotted as a function of the length of the A block. As can be seen in Fig. 6, N_{agg} increases significantly with increasing length of the A block. This is consistent with a commonly known trend that the micelle size increases with

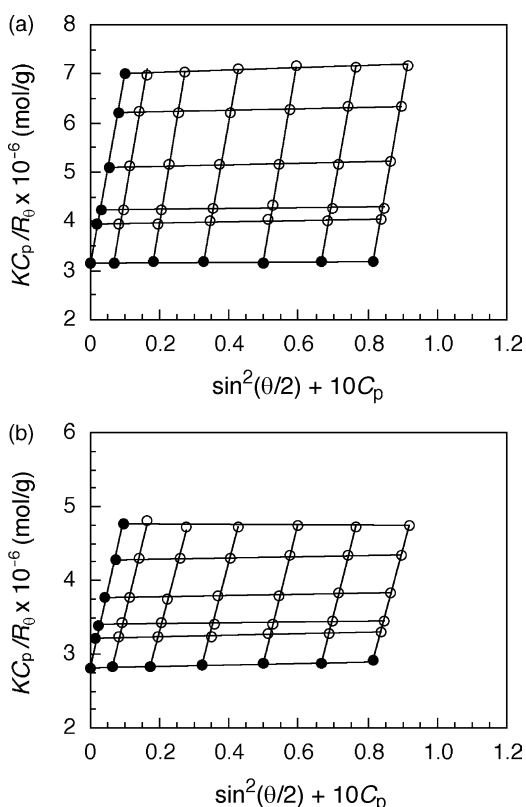


Fig. 5. Zimm plots for **b-Q57A50** measured in 0.10 M NaCl at pH 2.0; (a) and 10.0 (b).

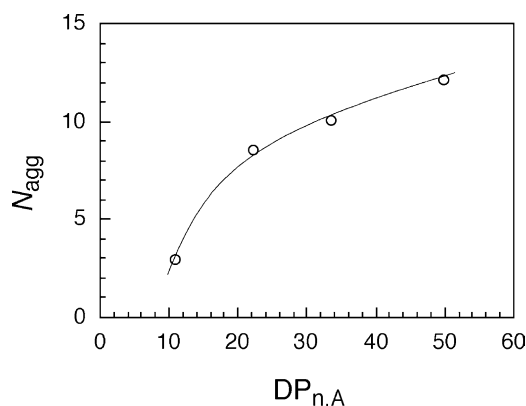


Fig. 6. Aggregation number plotted as a function of length of the A block.

increasing length of a hydrophobic block in amphiphilic diblock copolymers [23–26]. Values of N_{agg} for **b-Q57Am** are much smaller than those for micelles of other block copolymers such as poly(sodium acrylate)-*b*-poly(styrene) [25]. This may be because the A block is less hydrophobic even under basic conditions since it has dimethylamino groups. Similarly lower N_{agg} values have been reported for cationic block copolymers of [3-(methylamino)propyl]trimethylammonium chloride and 2-(diethylamino)ethyl methacrylate [10]. In the case of **r-Q55A57**, N_{agg} was determined to be ca. 1 at pH 10.0, indicative of a unimeric state.

3.4. Fluorescence

The formation of micelles by the block copolymers at pH 10.0 was investigated by a fluorescence probe technique with use of *N*-phenyl-1-naphthylamine (PNA) as a probe. PNA is known to be highly sensitive to its surrounding polarity, with the emission maximum shifting toward shorter wavelengths in response to a decrease in the micropolarity [27,28]. In Fig. 7(a), emission maxima for PNA fluorescence in the presence of the block copolymers and the reference random copolymer are plotted as a function of C_p . For all the copolymers, the emission maxima are practically constant at ca. 480 nm at $C_p \leq 10^{-3}$ g/L, indicating that PNA molecules exist in the bulk water phase in this low C_p regime. As C_p is increased, the emission maxima for all the block copolymers shift to shorter wavelengths in the C_p range 10^{-3} – 10^{-1} g/L, and this blue shift levels off at $C_p > 10^0$ g/L. This blue shift is due to the sequestration of PNA in the hydrophobic microdomains formed by association of dehydrated A blocks (i.e. the micelle core). Therefore, the plots in Fig. 7(a) indicate that PNA molecules in the bulk water phase are progressively solubilized in the micellar phase with increasing polymer concentration in the C_p range 10^{-3} – 10^{-1} g/L, with essentially all PNA molecules being solubilized at $C_p > 10^0$ g/L. Thus, the saturated values of the blue shifted emission maximum reflect hydrophobicity of the micellar core. The emission maximum for **r-Q55A57** also shifts to a shorter wavelength, showing a saturation at ca. 420 nm at $C_p > 10^{-1}$ g/L. Taken together with the light scattering data, it can be concluded that the random copolymer forms a unimeric micelle at basic pH.

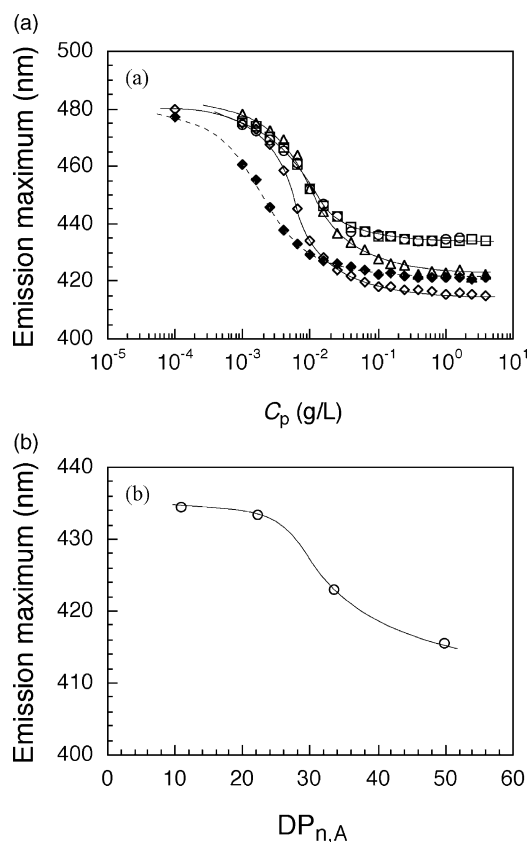


Fig. 7. Emission maximum plotted as a function of the polymer concentration for **b-Q57A11** (open circle), **b-Q57A22** (open square), **b-Q57A34** (open triangle), **b-Q57A50** (open diamond), and **r-Q55A57** (solid diamond) (a), and emission maximum plotted as a function of length of the **A** block at $C_p = 10^0$ g/L (b).

From the data in Fig. 7(a), the ratios of the PNA concentrations in the micellar phase and in the aqueous phase ($[PNA]_m/[PNA]_w$) were calculated from the following equation:

$$\frac{[PNA]_m}{[PNA]_w} = \frac{(\text{emission maximum}) - (\text{emission maximum})_{\min}}{(\text{emission maximum})_{\max} - (\text{emission maximum})} \quad (3)$$

Here, $(\text{emission maximum})_{\min}$ and $(\text{emission maximum})_{\max}$ are the minimum and maximum values for the emission maximum that can be estimated from Fig. 7(a). Plots of $[PNA]_m/[PNA]_w$ against C_p did not exhibit any onset C_p at which $[PNA]_m/[PNA]_w$ increased abruptly (data not shown). This observation indicated that the critical micelle concentrations were too low to be determined for all the copolymers examined.

In Fig. 7(b), the emission maximum at $C_p = 10^0$ g/L is plotted as a function of the length of the **A** block. As is clear in Fig. 7(a), the blue shift is maximized at this polymer concentration. With increasing length of the **A** block, the emission maximum decreases significantly near $DP_{n,A} = 22$. These data suggest that the micellar core is more hydrophobic for block copolymers having longer **A** block. Comparing the extent of the blue shift observed for **b-Q57A50** with that for **r-Q55A57**, it can be concluded that hydrophobic

microdomains in the block copolymer micelle are more hydrophobic than those in the random copolymer micelle.

4. Conclusion

A series of block copolymers of **Q** and **A** monomers, composed of a fixed **Q** block length of $DP_{n,Q} = 57$ and different **A** block lengths, ranging $DP_{n,A} = 11-50$ (**b-Q57Am**), were prepared by the RAFT technique and their pH-dependent micellization was studied by potentiometric titration, ^1H NMR spectroscopy, dynamic and static light scattering, and fluorescence spectroscopy. A random copolymer of **Q** and **A** (**r-Q55A57**) was also prepared by the RAFT technique and the micellization properties were compared with those of a block copolymer having a similar molecular weight and copolymer composition (**b-Q57A50**). At acidic pH, the **A** units are fully protonated and all the copolymers behave as simple polycations and exist in their unimeric state. On the other hand, at basic pH, the **A** units are deprotonated into hydrophobic tertiary amines and thus the copolymers formed micelles composed of hydrophilic **Q** units and hydrophobic **A** units. It is likely that the block copolymers form a core-corona type polymer micelle. Light scattering data for the block copolymers indicated that the R_h and N_{agg} for the core-corona micelle increased with increasing length of the **A** block. Fluorescence data obtained by use of PNA probe molecules indicated that the micellar core of the block copolymers with longer **A** block lengths was more hydrophobic. In the case of **r-Q55A57**, $N_{\text{agg}} \sim 1$ was confirmed by static light scattering. Hydrophobic microdomains in the unimolecular micelle formed by **r-Q55A57** were found to be less hydrophobic than the core of the micelle formed by **b-Q57A50**.

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