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SELF-ASSEMBLED AND NANOSTRUCTURED COPOLYMER AGGREGATIONS OF THE TERTIARY AMINE METHACRYLATE BASED TRIBLOCK COPOLYMERS

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The micellization behavior of novel tertiary amine methacrylate-based ABA type triblock copolymers formed by poly[2-(dimethylamino)ethyl methacrylate] [PDMA] middle block and poly[2-(diethylamino)ethyl methacrylate] [PDEA] or poly[2-(diisopropylamino)ethyl methacrylate] [PDPA] side blocks, $PDPA_m$-b-$PDMA_n$-b-$PDPA_l$, and $PDEA_m$-b-$PDMA_n$-b-$PDEA_l$ was investigated. Both types of triblock copolymers were water-soluble and had potential for various applications due to their self-assembled and the bottom-up nanoscale micellar construction. The micellar aggregations of the triblock copolymers in aqueous solutions with varying comonomer ratios, molecular weights, temperatures, and pH values were investigated by small-angle X-ray scattering and dynamic light scattering. Compact micellar aggregations were obtained as 0.5 weight percent solutions at 20–21°C and pH 8.67 to 9.05, and characterized as polydispersed spherical core-shells. One group of triblock copolymer micelles had PDPA-cores with radii from 18 to 21 Å and PDMA-shell thicknesses of 89–105 Å, whereas the other group had PDEA-core spherical micelles with core radii of 60–62 Å and a PDMA-shell thicknesses of 64–66 Å.

Keywords: Block copolymer; DLS; Dynamic light scattering; Micelles; SAXS; Small-angle X-ray scattering

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INTRODUCTION

The synthesis and micellization of hydrophilic block copolymers and their derivatives are used in the pharmaceutical, agricultural, and cosmetic industries with supercritical fluid technologies and nanoscale engineering. Hence, these triblock copolymers have gained great attention. In addition to their environmentally-friendly processing and practical applications, they are useful (Pillai and Panchagunia 2001; Anderson and Mallapragada 2002; Özcan et al. 2013). In the recent studies, the nanoscale diblock copolymer morphologies related with water-soluble copolymers based on tertiary amine methacrylates have been also investigated by light and X-ray scattering to provide bottom-up micellar construction and understanding and variation of their structures due to their responsive nature (Honeker et al. 2000; Putnam et al. 2007; Özcan et al. 2013).

Dynamic light scattering (DLS) and small-angle X-ray scattering (SAXS) may be employed for determining the structure of the aggregates and for investigating their interactions (Pedersen 1999). Hence, nanoscale structural information regarding block copolymer micelles, shapes, sizes, distributions, electron densities, and assembly state in solution may be defined and used to explain the correlation between structure and function of the developed micelles.

Stimuli-responsive diblock copolymers based on tertiary amine methacrylates were reported to be surface active and their solution behaviors were investigated in detail by Bütün et al. (Bütün, Billingham, and Armes 1997; Pedersen 1999; Honeker et al. 2000; Banez et al. 2001; Bütün, Armes, and Billingham 2001; Anderson and Mallapragada 2002; Liu et al. 2002; Yiqing et al. 2003; Putnam et al. 2007; Bütün, Taktak, and Tuncer 2011; Manet et al. 2011). A self-explanatory example is the diblock copolymers, which consist of hydrophilic [2-(dimethylamino) ethyl methacrylate] [DMA] and base-hydrophobic [2-(diethylamino)ethyl methacrylate] [DEA] or [2-(diisopropylamino)ethyl methacrylate] [DPA] monomers, which can selectively form micelles when the solution pH is above 7.0 (Bütün, Billingham, and Armes 1997; Bütün, Armes, and Billingham 2001).

Similarly, their ABA type triblock copolymers having PDMA blocks in the middle form flower-like micelles by side blocks forming hydrophobic micelle cores under basic conditions (Taktak and Bütün 2010). These triblock copolymers are water-soluble at acidic pH due to protonation of all tertiary amine groups, which causes hydration of all blocks. Thus, the triblock copolymer may dissolve in aqueous solutions as unimers due to ion-dipole attraction and behaves as polyelectrolytes. Upon an increase in the pH above 7, deprotonation of the side chains causes the PDEA and PDPA block to be dehydrated and to become hydrophobic due to steric effect of the two ethyl groups (Özcan et al. 2013). As a result, two groups of the copolymer may form flower-like micelles by PDEA blocs or PDPA blocks forming micelle core, whereas the middle PDMA blocks form the hydrated micellar-shell (Banez et al. 2001; Liu et al. 2002; Taktak and Bütün 2010).

In our previous study (Özcan et al. 2013), we investigated core-shell structure of AB type tertiary amine methacrylate based diblock copolymer micelles. Herein, we report light scattering investigation of flower-like micellization of ABA and CBC type tertiary amine methacrylate based triblock copolymers in which poly[2-(dimethylamino)ethyl methacrylate] [PDMA] was chosen as the hydrophilic

middle-block and the poly[2-(diethylamino)ethyl methacrylate] [PDEA] and poly[2-(diisopropylamino)ethyl methacrylate] [PDPA] block were employed as hydrophobic side blocks at pH above 7.0. Two groups of related triblock copolymers were designated to be $PDPA_m$-$PDMA_n$-$PDPA_l$ and $PDEA_m$-$PDMA_n$-$PDEA_l$.

The structure of the micelles were studied by small-angle scattering methods, using neutrons (SANS) and X-rays (SAXS), which are common powerful tools for the characterization of micelles in solution. The advantage of SANS and SAXS in comparison to light scattering is that they are more sensitive to internal structure of the scattering object. The scattering curves are governed by the shape, size, and polydispersity of the scattering objects and their contrast with respect to the solvent. Using SAXS and SANS, micelles may be described in a detailed way, including the properties of the hydrophobic core and the hydrophilic shell regions (Manet et al. 2011). The micelle size extracted from SAXS based on a flower-micelle model, however, was underestimated compared to the DLS results. In this study, the dependence of the micellization behavior of $PDPA_m$-*b*-$PDMA_n$-*b*-$PDPA_l$ and $PDEA_m$-*b*-$PDMA_n$-*b*-$PDEA_l$ triblock copolymer was investigated as a function of molecular weight, concentration, *n/m/l* ratio of the copolymer, and the pH of the aqueous solutions. When the micelle size and polydispersity values were measured, the DLS and SAXS results were consistent.

SMALL-ANGLE X-RAY SCATTERING MODEL

The analytical expressions for the model (spherical core-shell micelle) form factors and structure factors are provided as follows. SAXS intensity distribution for colloidal particles may be modelled by:

$$I(Q) = n_p P(Q) S(Q) \tag{1}$$

where each term may characterized using the intensity distribution function, $I(Q)$; the number density, n_p; the form factor, $P(Q)$; and structure factor, $S(Q)$. The function of the momentum transfer $Q = 4\pi\lambda^{-1}\sin\theta$, where 2θ is the scattering angley and λ is the wavelength of the incident X-ray beam. The $S(Q)$ is close to unity and may be disregarded for dilute solutions with minimal interparticle interactions (Chen and Lin 1987; Putnam et al. 2007). Subsequently, the zero-angle scattering intensity at $Q = 0$ may simplified to:

$$I(0) = (C - C_0) N V_{dry}^2 (\rho_p - \rho_o)^2 \tag{2}$$

for the copolymer concentration, C; critical micelle concentration, C_o; aggregation number, N; the volume of the copolymer, V_{dry}; and the scattering length densities of the copolymer and solvent, ρ_p and ρ_o (for water $\rho_o = 9.43 \times 10^{-6}$ Å^{-2} or 0.337 e$^-$/Å^3) (Svergun 1992; Svergun 1999; Hansen 2000; Yiqing et al. 2003; Kline 2006). The aggregation number may be obtained from the measured $I(0)$ value. Moreover, the form factor $P(Q) = |F(Q)|^2$ for monodisperse core-shell micelles is provided by:

$$F(Q, R_c, R_H) = \frac{4}{3}\pi\left[R_c^3(\rho_c - \rho_s)F_0(QR_c) + R_H^3(\rho_s - \rho_o)F_0(QR_H)\right] \tag{3}$$

where $F_0(x) = 3x^{-3}(\sin x - x\cos x)$ with $x = QR_c$ or QR_H. In this equation, R_c is the core radius: the micellar radius $R_H = R_c + t$ with the shell thickness t (Figure 1).

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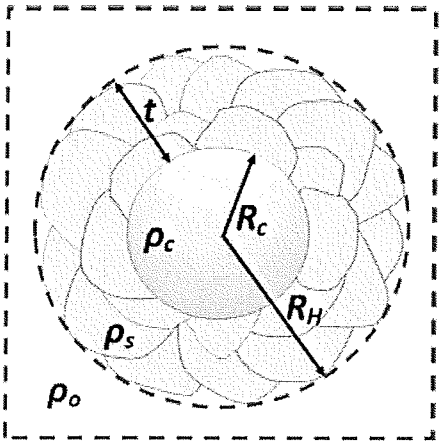

Figure 1. Schematic of a spherical core-shell flower micelle.

The core and shell scattering length densities are ρ_c and ρ_s. Additionally, SAXS intensity profile becomes $I(Q) = \langle n_p \rangle \langle P(Q) \rangle$ with the polydispersity in micellar size taken into consideration and the averaged form factor $\langle P(Q) \rangle = \langle P(Q,r) f(r) \rangle$. The number density of the scattering particles $n_p(r) = \langle n_p \rangle f(r)$ is described by the mean number density $\langle n_p \rangle$ and the Schultz size-distribution function (Sheu 1992):

$$f(r) = \left(\frac{z+1}{r_a}\right)^{z+1} r^z \exp\left[-\left(\frac{z+1}{r_a}\right) r\right] \Big/ \Gamma(z+1) \tag{4}$$

with $z > -1$, and the mean size, r_a; width parameter, z; and the polydispersity, $p = (z+1)^{-1/2}$. We used the same polydispersity for the core and micelle sizes to simplify the expression. A spherical core-shell flower micelle with the described structural parameters was represented by the core radius (R_c), shell thickness (t), micelle radius ($R_H = R_c + t$), and the scattering length densities of the core ρ_c, shell ρ_s, and solvent ρ_o in Figure 1.

Micelle size may be determined as well from the gyration radius (R_g) that is found from the model-independent Guinier approximation:

$$I(Q) \propto \exp\left(-R_g^2 Q^{2/3}\right) \tag{5}$$

in the low-q regime ($R_g Q \lesssim 1$) of a SAXS profile (Chen et al. 1987).

EXPERIMENTAL

Sample Preparation

A series of first group of the (PDPA$_m$-*b*-PDMA$_n$-*b*-PDPA$_l$) triblock, with *n/m/l* values *12/78/10, 15/75/10* and molecular weights ranging from ~35750 and ~56390, and also the second group of the (PDEA$_m$-*b*-PDMA$_n$-*b*-DEA$_l$) triblock, with *n/m/l* values *15/69/16, 22/62/16* and molecular weights (M_w) ranging from approximately 32,500 and 41,500, were synthesized as described previously (Bütün, Armes, and

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Table 1. Characterization triblock copolymers

Copolymer group	Sample code	Triblock copolymer	Molecular weight (g mol^{-1})	pH	Temperature (°C)	Polydispersity Index
I	F14	PDPA12-PDMA78-PDPA10	35750	8.95	20.0	0.10
	F15	(A - B - A)	47700	9.02	21.0	0.14
	F16		56390	9.05	20.2	0.24
	F17	PDPA15-PDMA75-PDPA10 (A - B - A)	44840	9.02	20.0	0.16
II	F10	PDEA22-PDMA62-PDEA16 (C - B - C)	41040	8.67	20.1	0.04
	F11	PDEA15-PDMA69-PDEA16 (C - B - C)	32155	8.68	20.8	0.08

A, PDPA, poly[2-(diisopropylamino)ethyl methacrylate]; B, PDMA, poly[2-(dimethylamino)ethyl methacrylate]; C, PDEA, poly[2-(diethylamino)ethyl methacrylate].

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Billingham 2001). The samples were dissolved in aqueous solution at concentrations of 5 mg/mL (0.5 wt%) and micellization was first indicated by the color transition of the sample solutions from transparent to blue before SAXS and DLS measurements. At 21–23°C, block copolymer samples of various concentrations were dissolved in aqueous solutions at pH of *ca.* 2–3 by HCl addition, followed by the addition of KOH for the final solution pH values (8.67–9.05) and micellization of the block copolymer (Özcan et al. 2013).

The samples were identified and coded as shown in Table 1. In the first group, F14-F16, the samples had the same *l,* comonomer ratio *m/n/l,* temperature (T), and pH. The F17 sample had the same PDPA core as F14-F16 but the comonomer ratio and molecular weight were different to investigate stability of the micelle forms. In the second group, PDEA polymeric units were expected as micelle core structures because of their hydrophobic properties (Yiqing et al. 2003). Both samples in this group had the same monomer *l* value of PDEA but different monomer ratios and molecular weights.

Small-angle X-Ray Scattering

The samples in solution forms were exposed 0.5 mm beam (15 keV) at the 23A1 IASW-Small/Wide Angle X-Ray Scattering beamline, National Synchrotron Radiation Research Center (NSRRC). Transmission data was measured by using the sandwiched solution between two capton film sheets that were sealed to avoid evaporation. The gap between the two films was 1.5–1.9 mm and the X-ray exposure time was 100 s for each sample. The scale factor (499.67and 727.38), sample transmissions (0.78), and sample-detector distances (3311.616 mm) were determined for 15 keV energies. The X-ray beam was passed through a 0.5 mm pinhole to create a microbeam on the samples. Data was calibrated with silver behenate (orders of the 001 reflection at 1/5.838 nm^{-1}).

The SAXS data is illustrated in Figures 2 and 3. The observed broad peaks from 0.4 to 0.7 Å^{-1} indicate micellar formation in all samples. The F10, F11, and

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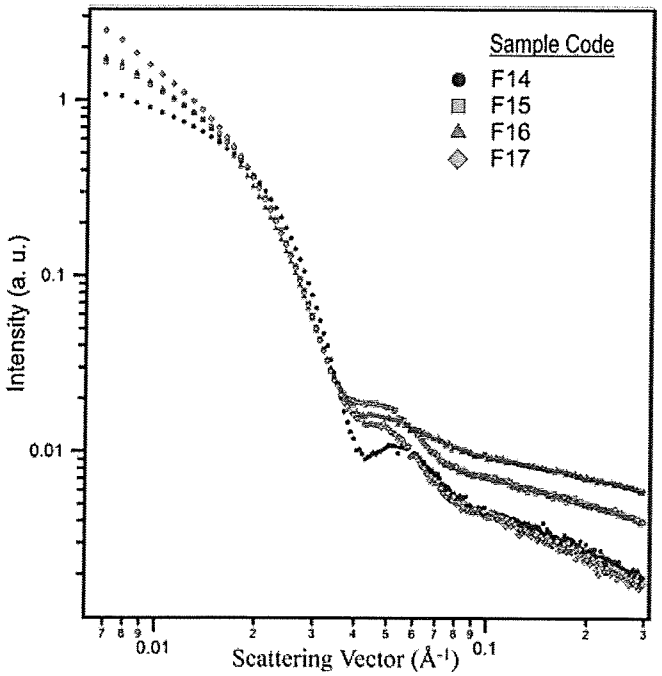

Figure 2. SAXS profiles of Group I.

F14 samples indicate more compact micellar aggregations from the SAXS profiles that display I(q) scattering intensity as a function of the q magnitude of scattering vector ($q = 4\pi\sin\theta/\lambda$, with 2θ the scattering angle).

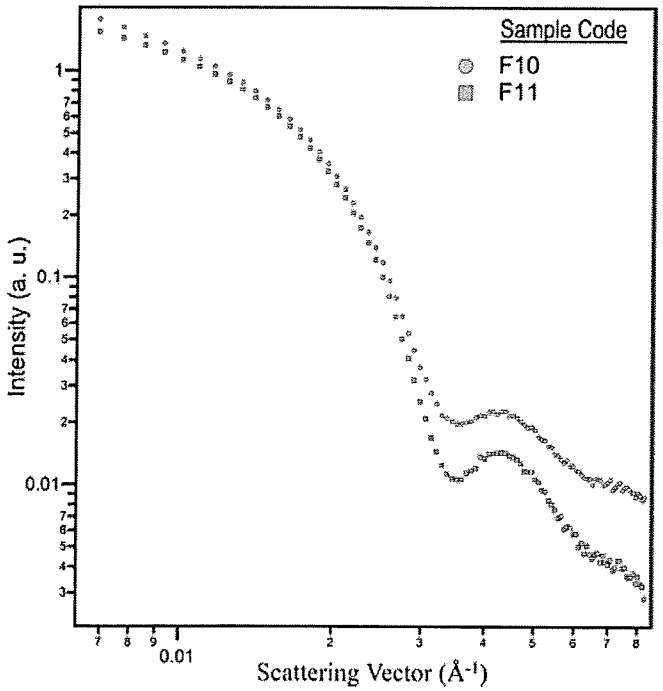

Figure 3. SAXS profiles of Group II.

Dynamic Light Scattering

Dynamic light scattering (DLS) was performed on 0.5 wt% copolymer solutions at 20.0–20.8°C using a Malvern ALV/CGS-3 goniometer system (with ALV/LSE-5003 Multi-8-serial collector, Cl0 ¼ 632.8 nm, 22 mV, Helium-Laser) (Özcan et al. 2013). The distribution and size of micelles were obtained from scattering peak widths and positions.

RESULTS AND DISCUSSION

The measured and calculated X-ray scattering intensities were fitted each other by using the polydisperse core-shell spherical model. IGOR Pro6 (Kline 2006), GNOM (Svergun 1992) and DAMMIN (Svergun 1999) programs were used to evaluate SAXS data and illustrate the results. The fit results of the polydisperse spherical core-shell model are shown in Figures 4, 5, 6, 7, and 8. The κ^2 values (1.3–2.9) were in the acceptable range (1–7) and showed the convenience of the model. The measured scattered wave amplitude and intensity related with reciprocal space were Fourier transforms of radial electron density and distance distribution function, respectively, defined for real space. Moore's Indirect Fourier Transform Method (Hansen 2000) has been also used to determine real space pair distance distributions of the micelles. The paired distance distributions (PDDs) also provided homogenous micelle distributions with a Gaussian peak for each sample. The maximum diameters of the micelles and radius of gyration values are also presented

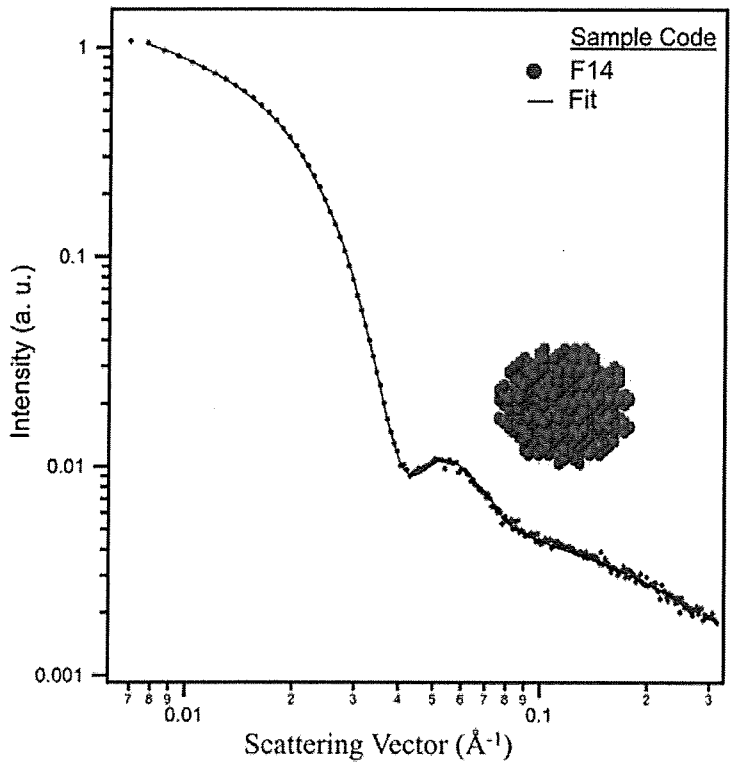

Figure 4. Fit views of the group-I and possible tridimensional shape of the compact micelles of F14.

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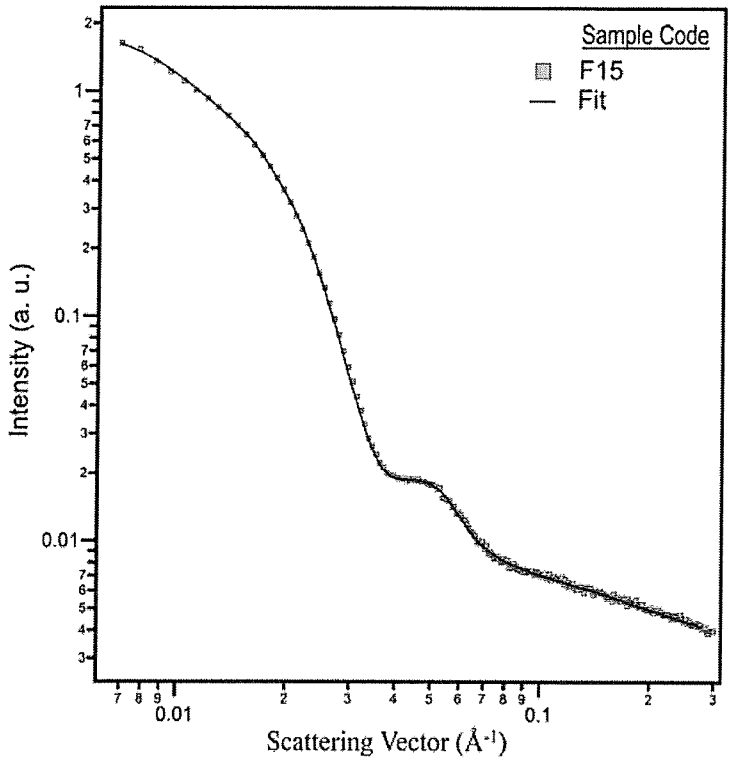

Figure 5. Fit view micelles of F15.

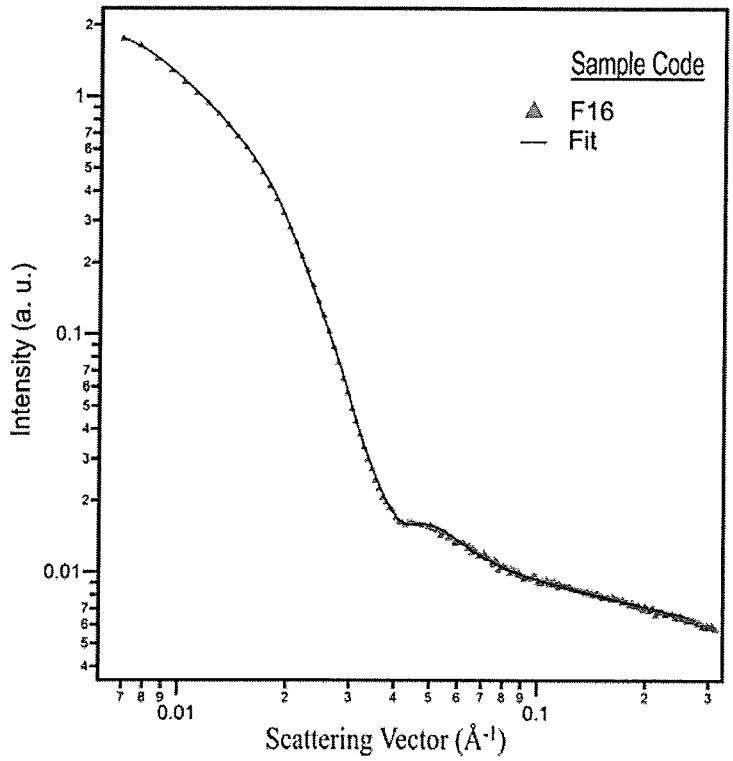

Figure 6. Fit view micelles of F16.

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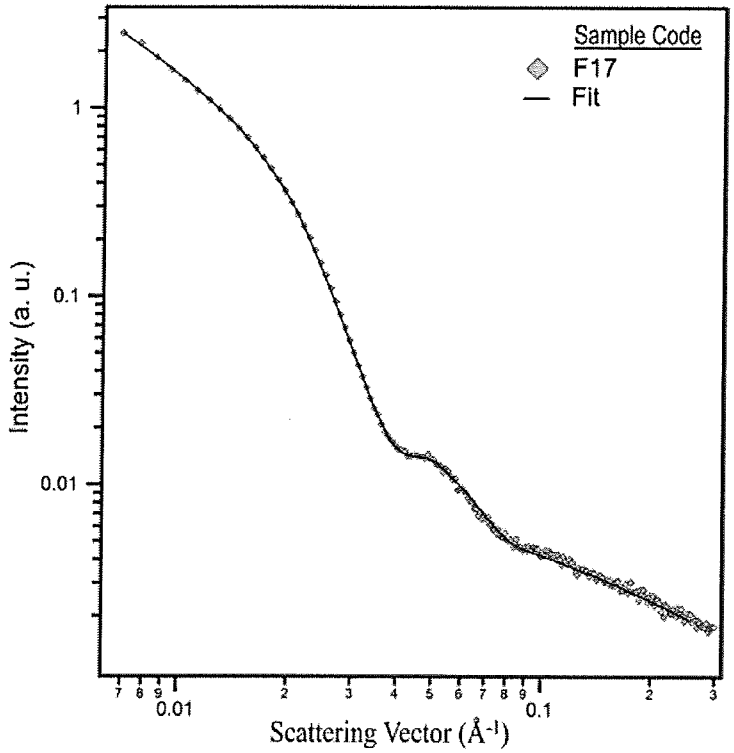

Figure 7. Fit view micelles of F17.

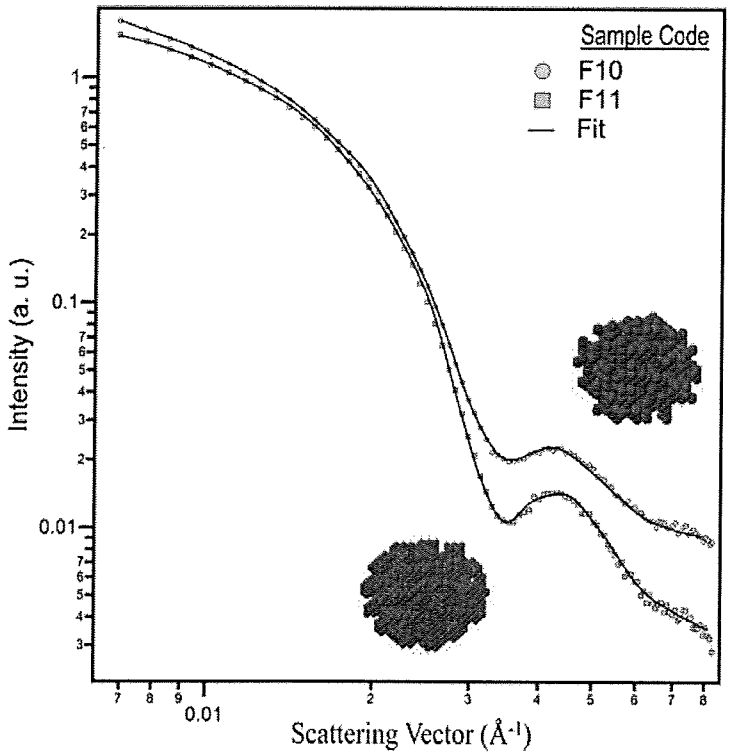

Figure 8. Fit views of the group-II and the tridimensional shapes of the compact micelles of F10 and F11.

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Table 2. Nanoscale structural parameters

Sample group	Sample code	Triblock copolymer	Molecular weight ($g\ mol^{-1}$)	Core density ($Å^{-2}$)	Shell density ($Å^{-2}$)	Core radius (Å)	Shell thickness (Å)	Micelle radius (SAXS) (Å)	Micelle radius (DLS) (Å)	Micelle radius (PDDs) (Å)	Maximum extend
I	F14	PDPA12-PDMA78-PDPA10 PDPA Core	35750	2.43×10^{-5}	1.84×10^{-5}	18	89	107	101	119	250
	F15		47700	2.61×10^{-5}	1.83×10^{-5}	21	95	116	135	139	350
	F16		56390	2.74×10^{-5}	1.81×10^{-5}	19	98	117	146	158	395
	F17	PDPA15-PDMA75-PDPA10 PDPA Core	44840	2.72×10^{-5}	1.12×10^{-5}	19	105	124	145	154	359
II	F10	PDEA22-PDMA62-PDEA16 PDEA Core	41040	1.31×10^{-5}	1.51×10^{-5}	60	64	124	109	143	348
	F11	PDEA15-PDMA69-PDEA16 PDEA Core	32155	1.41×10^{-5}	1.62×10^{-5}	62	66	128	114	140	306

PDPA, poly[2-(diisopropylamino)ethyl methacrylate]; PDMA, poly[2-(dimethylamino)ethyl methacrylate]; PDEA, poly[2-(diethylamino)ethyl methacrylate].

in Table 2. The maximum extent values were approximately equal to the diameters of the compact micelles as expected. These values are also evidence of freely moving (not colloidal) micelle distributions. The micelles have close to spherical symmetry with core-shell structures and outer layers that may be described as flower leaves, and hence the nanoaggregations in solution may be named as flower micelles (McCormick et al. 2008).

The micellar size and polydispersity index values obtained from SAXS were consistent with those obtained by DLS as seen in Table 2. The packing micelles of the first group of the $PDPA_m$-*b*-$PDMA_n$-*b*-$PDPA_l$ and the second group of $PDEA_m$-*b*-$PDMA_n$-*b*-$PDEA_l$ triblock copolymers in aqueous solutions were characterized by the structural information shown in Table 2.

The information shown in Table 2 is a quantitative explanation of the micelles in the framework of polydisperse simple core-shell spherical model. Three-dimensional views are presented by the pink balls in Figures 4, 5, 6, 7, and 8, whereas

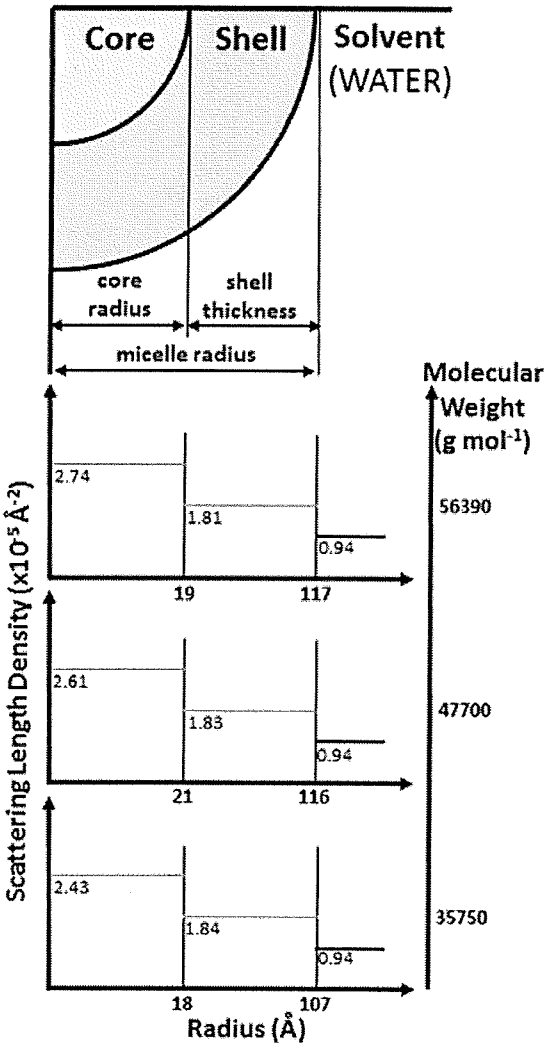

Figure 9. Quantitative results for the F14, F15, and F16 copolymers at 21°C and pH 9. Electron densities were along radial axis of the micelles and the structural changes were in respect to molecular weight.

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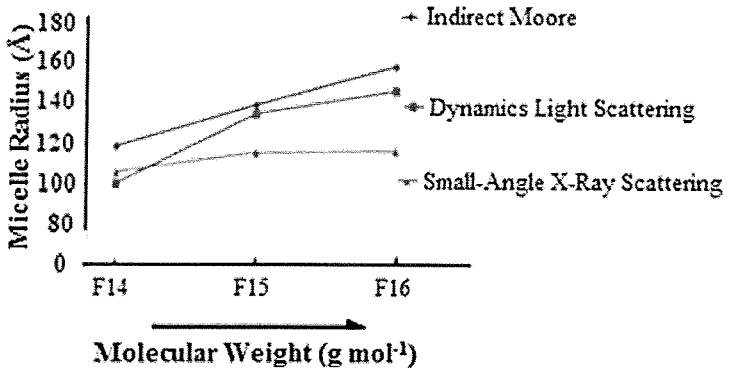

Figure 10. The changes of hydrodynamic radii in respect to molecular weight.

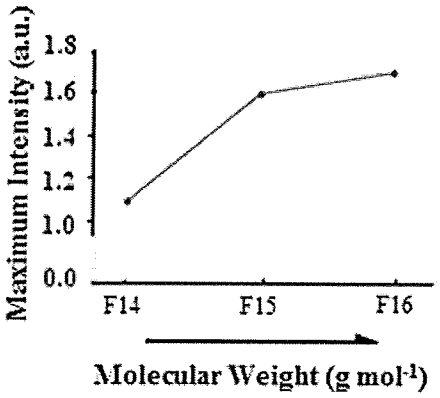

Figure 11. Effect of molecular weight on maximum scattering intensities.

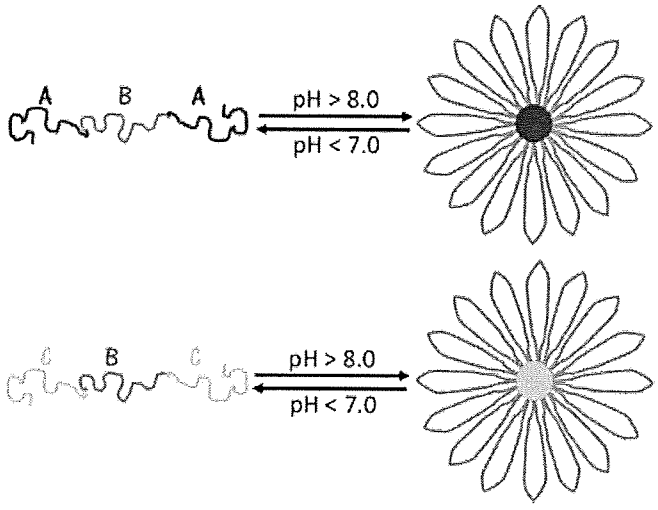

Figure 12. The shapes of flower micelles: A, poly[2-(diisopropylamino)ethyl methacrylate]; B, poly[2-(dimethylamino)ethyl methacrylate]; and C, poly[2-(diethylamino)ethyl methacrylate].

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the model was used to establish the structure of the copolymer micelles. The flower-like micelle structures are also observable in these shapes. The leaves of the polymeric flowers may be also observable in these models. Quantitative results are clarified by using some figures and graphics in the content of shown in Figures 9, 10, and 11.

All of the samples had spherical core shell micelle aggregations. The shapes of the micelles were defined as flower micelles. Molecular models of these aggregations are presented in Figure 12.

CONCLUSIONS

The micellization behaviors of the ($PDPA_m$-*b*-$PDMA_n$-*b*-$PDPA_l$) and ($PDEA_m$-*b*-$PDMA_n$-*b*-$PDEA_l$) triblock copolymers were successfully studied by SAXS and DLS. When the solutions were prepared by direct solvation of these block copolymers in aqueous media, the formation of aggregates was displayed by several techniques. The micelle sizes performed from the SAXS and DLS studies are compatible. The triblock copolymers formed micelles with aggregation numbers depending linearly on the *n*/*m*/*l* ratios at 20–21°C from pH of 8.67–9.05. Three dimensional views of the compact micelles are shown in Figures 4–8. The structures of the copolymer micelles described by the polydisperse simple core-shell spherical model to be flower-shape micelles. The views of F10 and F11 were better than the three-dimensional structures of the compact micelles of F14. Although the molecular masses of copolymers were approximately the same, the PDEA-core structure was more compact micelles than the PDPA-core micellar system. As a result, compact micelles that are depended on the radius and thickness have been reported. The core shell structure allows estimation of the effective hydrophobic/hydrophilic junction area radii and hydrophobic lengths of the copolymer spherical micelles. The results may have applications as pharmaceutical carriers based on tertiary-amine-methacrylate-based block copolymers.

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