

Synthesis and properties of acrylate-acrylic acid-acrylate triblock copolymers with gemini structure by RAFT polymerization

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ABSTRACT: A class of gemini structure block copolymers with a trithiocarbonate ester spacer group had been synthesized with S, S'-bis (R, R'-dimethylacetic acid) trithiocarbonate as reversible addition fragmentation chain transfer agents and acrylic acid as the second monomer. These triblock copolymers were characterized by ¹H NMR spectroscopy, gel permeation chromatography in terms of their compositions, molecular weights and behaviour at the air-water interface. The results showed that the weight-average molecular weight was larger than theoretical molecular as the acrylate side chain increased. The polymer neutralized by sodium hydroxide solution had low critical micelle concentration which was $<10^{-2}$ mol L⁻¹ in water. TEM and DLS showed that it formed a special micelle structure with large pore structure which might lead to low surface tension and critical micelle concentration in water. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43017.

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INTRODUCTION

Gemini surfactants contain two identical amphiphilic moieties which are connected at the level of head groups by a spacer.¹ Over the past decades, gemini surfactants have attracted considerable amount of interests for its unique and superior properties compared with conventional surfactants in many aspects such as lower critical micelle concentration (CMC), greater efficiency in lowering the surface tension in water. They hold great application potential such as wetting agents, drug entrapment and release, enhanced oil recovery and even in gene therapy.²

In the area of gemini surfactants, cationic, anionic, nonionic compounds have been widely investigated. However, there were few reports about block polymeric gemini surfactants. There were two reasons for this: (1) the polymerization often yielded a set of mixture with traditional polymerization method. In other words, polymerization product contained polymer with different molecular weight and a large polydispersity index (PDI); (2) appropriate linking groups that balanced comprehensive properties were difficult to find and select.

Reversible addition fragmentation chain transfer (RAFT) polymerization was a new type of living radical polymerization which was developed in past two decades.^{3,4} RAFT technique could technically solve the above mentioned problems for its well-known advantages of yielding well-defined polymerization structure and low PDI. Along these lines, in the work reported here the amphiphilic acrylate-acrylic acid-acrylate triblock copolymers were synthesized by RAFT polymerization with trithiocarbonates to synthesize particular structure (Figure 1) as gemini surfactants. The designed gemini surfactant contained several hydrophobic groups and hydrophilic groups in the polymer chain, connected by a linkage close to the hydrophilic groups.⁵ RAFT polymerization⁶ has become a convenient tool to synthesize various (co)polymers with controlled molecular weight, narrow PDI and well-defined chain structure⁷ as controlled/living radical polymerization (CLRP). Compared with the other two CLRPs, nitroxide-mediated polymerization (NMP)⁸ and atom transfer radical polymerization (ATRP),⁹ RAFT polymerization has distinct advantages, including mild reaction condition, the compatibility with a wide range of monomer types and monomer functionality.¹⁰⁻¹³

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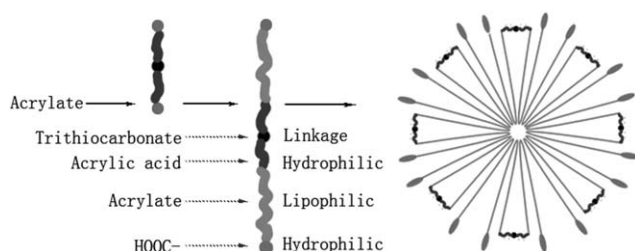


Figure 1. Example of acrylate-acrylic acid-acrylate synthesized by RAFT polymerization and micelle structure.

RAFT polymerization has become important technique in diagnosis and treatment of infectious and genetic diseases for that it allowed unprecedented latitude in synthesis of water soluble architectures with precise dimensions and appropriate functionality for conjugation and targeted delivery of diagnostic and therapeutic agents.¹⁴ It is apparent that when compared with more conventional processes currently utilized, the synthetic control afforded by the RAFT process and the resulting facile post-polymerization functionalization are advantageous and the surfactants we have synthesized are different with other normal polymer surfactants as for their gemini structure. It is very necessary to develop novel amphiphilic polymer micelles or vesicles.

In order to obtain block copolymers whose PDI was better controlled, we turned to RAFT polymerization,^{15–18} which allowed good control of functionality and polydispersity. More importantly, trithiocarbonate ester could be the appropriate spacer group for the designed polymeric gemini surfactants (Figure 1). In the work reported here, we reported a facile synthesis of block copolymer of acrylate and acrylic acid (AA) via controlled polymerization technique RAFT in solution. The resulting triblock copolymers were systematically characterized by ¹H NMR, GPC, and tensiometer. The advantage of our approach was that we choose the trithiocarbonate ester as Gemini spacer group and RAFT allows well controlled molecular weight, PDI and surface property using different acrylate. A series of different acrylate were studied and narrow polydispersity (PDI < 1.40) for polymeric gemini surfactants triblock copolymers had been successfully prepared. Finally, low CMC (< 10⁻² mol L⁻¹) and micelle structure of these block polymer neutralized with sodium hydroxide solution was observed.

EXPERIMENTAL

Materials

Methyl acrylate (MA, Aldrich, 99%), butyl acrylate (BA, Aldrich, 99%), isooctyl acrylate (IA, Aldrich, 99%), lauryl acrylate (LA, Shanghai Aoke Ltd., 99%) and tetradecyl acrylate (TA, Shanghai Aoke Ltd., 99%) were washed three times with 5 wt % sodium hydroxide (NaOH) aqueous solution to remove the inhibitor, followed by washing thoroughly with deionized water until the aqueous phase was neutral. AA (Aldrich, 99%) was distilled under reduced pressure prior to use. Ethyl acetate (Aldrich, 99%) was used as the solvent. S, S'-bis(R, R'-dimethylacetic acid) trithiocarbonate (BDAT) was synthesized according to the published procedure.¹² Azobisisobutyronitrile (AIBN, Aldrich, 99%) was used as initiator.

Nuclear Magnetic Resonance Spectroscopy (NMR)

¹H NMR samples were prepared by dissolving the corresponding amount of the surfactant in CDCl₃. ¹H NMR experiments were recorded on a Varian NMR-400 using 0.01 wt % of tetramethylsilane (TMS) as internal standard.

Gel Permeation Chromatography (GPC)

All the polymers that had been synthesized were characterized using GPC to determine their molecular weight and PDIs. For the polyacrylate and the triblock copolymers, GPC was performed on a Polymer Laboratories chromatograph equipped with an RID-10A refractive index detector and a Tskgel G3000PW column, calibrated using polystyrene (PSt) standards. The mobile phase was THF with a flow rate of 0.5 mL min⁻¹ using a Shimadzu LC-20AT HPLC pump and the testing temperature was set at 40°C. The molecular weight calibration curve was based on eight narrow PDI linear PSt standards (molecular weights of 589; 1010; 2500; 5620; 9490; 16,700; 37,200; and 98,900 g mol⁻¹) from TSKgel standards.

Equilibrium Surface Tension

The surface tensions of aqueous solutions of surfactant were measured with a Krüss K100 tensiometer by the Wilhelmy plate technique. Sets of measurements to obtain equilibrium surface tension were taken until the change in surface tension was less than 0.05 mN m⁻¹ every 10 min.

Transmission Electron Microscopy

TEM images were obtained with a JEOL JEM-2100 (HR) transmission electron microscope at a working voltage of 200 kV.

Particle Size

The particle-size distribution of the sample was determined by measuring the dynamic light scattering (DLS) (NICOMP 380 ZLS).

Synthesis of Poly Acrylate-Acrylic Acid-Acrylate (PMA-PAA-PMA, PBA-PAA-PBA, PIA-PAA-PLA, PLA-PAA-PLA, and PTA-PAA-PTA)

Methyl acrylate (43 g, 0.50 mol)/butyl acrylate (43 g, 0.34 mol)/IA (43 g, 0.23 mol)/LA (43 g, 0.18 mol)/tetradecyl acrylate (43 g, 0.16 mol), AIBN (0.43 g 2.62 mmol) and RAFT agent were dissolved in ethyl acetate (25 mL) in a 250 mL flask. The mixtures were thoroughly degassed 8 times before reaction for 10 min using a nitrogen flush stream. The reaction mixture was heated under argon at 75°C for 24 h, and then AA (Table I) and AIBN (0.2 g, 1.22 mmol) were added. Triblock copolymer was synthesized after another 40 h reaction under 75°C. The

Table I. The *M_n* and PDI of Different Acrylate-Acrylic Acid-Acrylate copolymers

Copolymers	AA/mol	<i>M_n</i> (mol/g)	Theory <i>M</i> (mol/g)	PDI	yield/%
PMA-b-PAA	0.126	4791	4783	1.30	80
PBA-b-PAA	0.126	7802	4604	1.13	76
PIA-b-PAA	0.126	6388	4665	1.19	77
PLA-b-PAA	0.168	8200	4411	1.40	69
PTA-b-PAA	0.210	9430	4506	1.32	67

Table II. ^1H NMR Spectroscopy of Triblock Copolymers

Triblock copolymer	^1H NMR (400 MHz, CDCl_3)
PMA-PAA-PMA	δ 3.60 (s, 3H, $-\text{CH}_3$), 2.34 (m, 1H, $-\text{CH}-$), 2.02 (m, 1H, $-\text{CH}_2-$), 1.65 (m, 1H, $-\text{CH}_2-$), 1.16 (m, 1H, $-\text{CH}_3$).
PBA-PAA-PBA	δ 3.98 (s, 3H, $-\text{CH}_2$), 2.32 (m, 2H, $-\text{CH}-$), 1.98 (m, 2H, $-\text{CH}_2-$), 1.60-1.50 (m, 3H, $-\text{CH}_2-$), 1.37-1.24 (m, 3H, $-\text{CH}_2-$), 1.23-1.01 (m, 1H, $-\text{CH}_2-$), 0.87 (t, $J = 7.2$ Hz, $-\text{CH}_3$).
PIA-PAA-PIA	δ 3.89 (s, 3H, $-\text{CH}_2$), 2.34 (m, 2H, $-\text{CH}-$), 2.04 (m, 2H, $-\text{CH}_2-$), 1.24 (m, 13H, $-\text{CH}_2-$), 0.82 (m, 10H, $-\text{CH}_3$).
PLA-PAA-PLA	δ 3.84 (s, 3H, $-\text{CH}_2$), 2.10 (s, 2H, $-\text{CH}-$), 1.98 (s, 1H, $-\text{CH}_2-$), 1.54 (s, 3H, $-\text{CH}_2-$), 1.20 (s, 30H, $-\text{CH}_2-$), 0.81 (d, $J = 6.5$ Hz, 5H, $-\text{CH}_3$).
PTA-PAA-PTA	δ 3.90 (s, 3H, $-\text{CH}_2$), 2.10 (s, 2H, $-\text{CH}-$), 1.98 (s, 1H, $-\text{CH}_2-$), 1.55 (s, 3H, $-\text{CH}_2-$), 1.20 (s, 33H, $-\text{CH}_2-$), 0.82 (d, $J = 5.4$ Hz, 5H, $-\text{CH}_3$).

polymerization was quenched by placing the flask in ice bath and distilled under reduced pressure at 40°C to remove excess solvent and unreacted monomer. The polymer was dried at 60°C for 5 h to calculate reaction yield. The structures were confirmed by ^1H NMR spectroscopy (See SI: Figures S-1 to S-5) and NMR data were summarized in Table II.

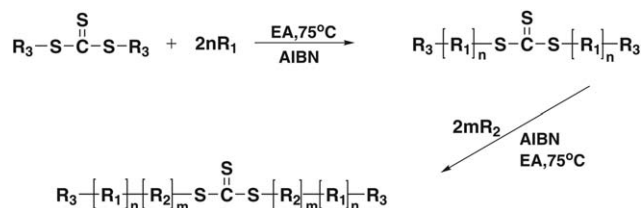
Preparation of Poly Acrylate-Sodium Acrylate-Acrylate (PMA-PAA-PMA, PBA-PAA-PBA, PIA-PAA-PIA, PLA-PAA-PLA, and PTA-PAA-PTA)

2 g triblock copolymers in 25 mL flask were distilled under reduced pressure at 40°C to remove excess solvent. Then 0.01 g mL^{-1} sodium hydroxide solution was added in the flask slowly and stirred until the pH was 7. Then the water was removed under vacuum and the PMA-PAA-PMA surfactants were obtained and stored under -10°C .

RESULTS AND DISCUSSION

Synthesis of Poly Acrylate-Acrylic acid-Acrylate Triblock Co-Oligomers

Ethyl acetate was chosen as the solvent as the solvent screening experiment showed that it could dissolve monomer, RAFT agent BDAT and AIBN fairly well. The reaction could be maintained through the reflux as the reaction temperature is close to ethyl acetate's boiling point. Another advantage was that the starting materials could react completely with low solvent content (35 wt %) through RAFT agent. The synthesis of acrylate-acrylic acid-acrylate triblock co-oligomers was carried out via sequential monomer polymerization (Figure 2). The acrylate-acrylic acid-acrylate triblock copolymers were neutralized with sodium hydroxide and water was used to remove unreacted AA moiety.

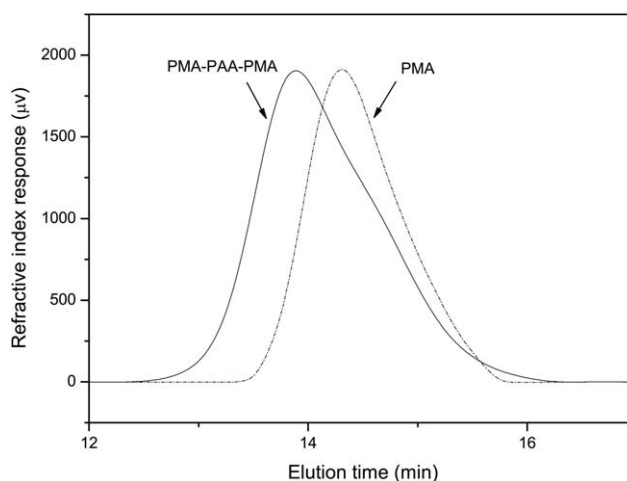
**Figure 2.** Synthetic routes of triblock copolymers via RAFT polymerization.

$\text{R}_1 = \text{CH}_2=\text{CHCOOCH}_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_3\text{CH}_3$, $\text{CH}_2=\text{CHCOOCH}_2\text{CH}(\text{CH}_2\text{CH}_3)(\text{CH}_2)_3\text{CH}_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{11}\text{CH}_3$, $\text{CH}_2=\text{CHCOO}(\text{CH}_2)_{13}\text{CH}_3$, $\text{R}_2 = \text{CH}_2=\text{CHCOOH}$, $\text{R}_3 = \text{C}(\text{CH}_3)_2\text{COOH}$

By choosing this sequence, the designed polymeric gemini surfactants was successfully synthesized with features of polyacrylic acid (PAA) attached to the trithiocarbonate as the hydrophilic chain and polyacrylate attached to the carboxyl end group as the core. The presence of the carboxylic acid end group as part of the corona assists the self-assembly of acrylate-acrylic-acrylate acid triblock copolymers to form micelle in an aqueous medium as the carboxylic acid end group was more water soluble.

The synthesis of acrylate-acrylic acid-acrylate triblock copolymers by RAFT allowed tuning surface activity for the hydrophilic lipophilic group chain length could be increased or decreased for a specific gemini surfactants, provides a new way for the design of amphoteric surfactants.

The controlled nature of the polymerizations in this study was also demonstrated in Figure 3 which displays the GPC traces of the PMA homopolymer and PMA-PAA-PMA. It could be observed that the GPC traces of the PMA-PAA-PMA were

**Figure 3.** GPC traces of the PMA and the daughter triblock copolymers PMA-PAA-PMA.

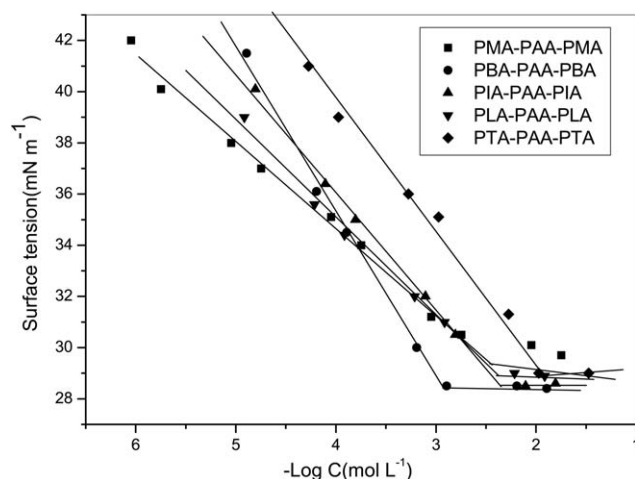


Figure 4. The surface tension of the polymeric gemini surfactant in water at 25°C.

shifted to shorter elution time and broadened relative to the parent macroRAFT agent PMA. The obtained final PDI was just a little higher than the PMA, which indicated that deactivated polymer generated during the synthesis of the macroRAFT agent PMA.¹⁹ The GPC traces revealed a single peak indicating recombination of the polymer chains and triblock copolymers were synthesized successfully.

Effect of Mw and PDI on Different Acrylate

The Mw and PDI of different acrylate were summarized in Table I. PDIs of the triblocks were determined by GPC to be <1.40, demonstrating that RAFT polymerization was a versatile tool to create triblock co-oligomers via sequential monomer polymerization. The theoretical molar weight could be calculated as follows:

$$M_{th} = \left(\frac{n_{Acrylate} M_{Acrylate}}{n_{RAFT}} + \frac{n_{AA} M_{AA}}{n_{RAFT}} + M_{RAFT} \right) \quad (1)$$

$$yield\% = \frac{m_{Acrylate} + m_{AA} + m_{RAFT}}{n_{RAFT}} yield\%$$

All obtained final M_n 's were higher than the theoretical values, which indicated that RAFT agent could not react completely. The M_n was found to increase with increasing chain length of acrylate. These results implied a better controlled character with lower chain length. Longer branches might result in entangled structures thus RAFT polymerization was disturbed.

Surface Tension and CMC in Water

Figure 4 showed the curve of the surface tension versus $-\log$ (surfactant molar concentration) for the gemini surfactant. The equilibrium values of surface tension were obtained in 1-2 h within the higher concentration region, whereas the longer equilibration time (5-7 h) was required in the area of lower concentration range.

For all analogs, within the low concentration, the surface tension of surfactant solution would dramatically decrease as the concentration increased and reached a breakpoint. Surfactant concentration which reached this breakpoint was assumed as the surfactant CMC. Several parameters could be obtained from the surface tension isotherm; CMC, surface tension at CMC (γ_{cmc}), the maximum surface excess concentration (Γ_{max}), the minimum area per molecule (A_{min}), the logarithm of surfactant concentration required to reduce the surface tension by 20 mN m^{-1} ($pC_{20} = -\log C_{20}$), CMC/ C_{20} . The minimum area per molecule, A_{min} , was calculated using the Gibbs equation²⁰ as follows:

$$\Gamma_{max} = \frac{1}{2.303nRT} \left(\frac{\partial \gamma}{\partial \log C} \right)_T \quad (2)$$

$$A_{min} = (N_A \Gamma)^{-1} \times 10^{16} \quad (3)$$

where $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$, $N_A = 6.02 \times 10^{23}$, $T = 318.15 \text{ K}$, Γ_{max} was in mol/cm^2 , and A_{min} was in $(\text{nm}^2/\text{molecule}) \times 10^2$. The parameter n represented the number of species at the interface whose concentration changed with surfactant concentration. For anion gemini surfactants $n = 3$ was chosen to compare A_{min} values within a series of compounds.

The relationship between CMC and PDI in the triblock copolymer could be established using data summarized in the Table III. γ_{cmc} was very low which was gemini characteristics and indicated that the designed and obtained polymer are indeed a series of Gemini surfactant. CMC values decrease with the decreasing PDI except for PTA-PAA-PTA. This could be due to the reason that the different molecular weight polymers produced antagonism, a smaller degree of dispersion makes the molecular weight distribution more narrow and easier to form a relatively uniform sized micelles. Generally speaking, the longer the branched chain, the higher CMC, but in our study of the polymeric Gemini surfactants, it showed that the branched structure couldn't follow the same trends.

In addition, the value of pC_{20} of PMA-PAA-PMA was quite larger than other copolymers. As pC_{20} also measures the efficiency of adsorption of surfactant at the air/water interface,

Table III. Surface Properties of Acrylate-Acrylic Acid-Acrylate copolymers in H_2O at 25°C

copolymers	CMC (mol L ⁻¹)	γ_{cmc} (mN/m)	$10^{10} \Gamma_{max}$ (mol/cm ²)	$10^2 A_{min}$ (nm ²)	pC_{20}	CMC/ C_{20}
PMA-b-PAA	3.55×10^{-3}	29.30	45.99	3.61	5.63	1520
PBA-b-PAA	1.20×10^{-3}	28.53	38.87	4.27	4.76	69
PIA-b-PAA	4.47×10^{-3}	28.55	38.87	4.27	4.90	355
PLA-b-PAA	4.27×10^{-3}	28.81	57.48	2.89	5.35	960
PTA-b-PAA	12.6×10^{-3}	28.80	73.91	2.25	4.10	159

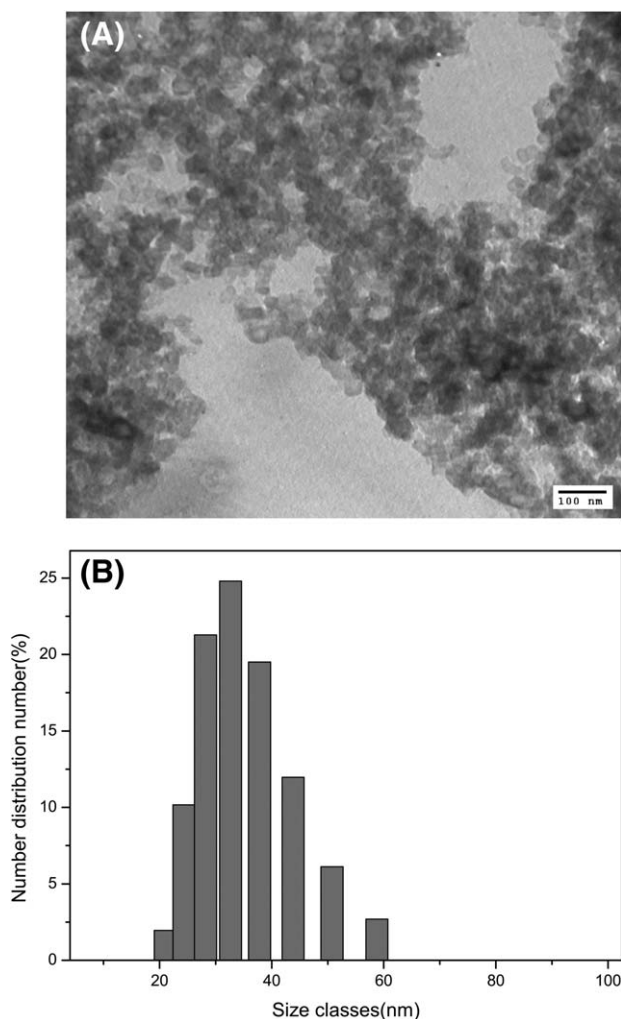


Figure 5. (A) TEM images and (B) DLS of PMA-PBAs-PMA in solution at 5CMC.

implied that longer hydrophobic chain leads to a better efficiency. These results were also supported by the CMC/C₂₀ ratio based on greater surfactant absorption at the air/water interface relative to the micelle formation. The CMC/C₂₀ ratio of PMA-PAA-PMA was much larger than other copolymers. This indicated that the adsorption at the air/water interface for the acrylate-acrylic acid-acrylate triblock copolymers is higher in comparison with others micellization in solution. The A_{min} values (per gemini molecule) for copolymers in water showed a maximum value in PBA-PAA-PBA. It was consistent with the trend of PDI as lower PDI led to higher value of A_{min}.

Structure of Micelles

It is well known that amphiphilic block polymers form micelles or reverse micelles when dissolved in selective solvents. Regular micelles are formed in aqueous or in high polarity solvents, while reverse micelles are formed in nonpolar or in low-polarity solvents.²¹ In this study, the aqueous was chosen, and, therefore, regular micelles were expected to form. Aqueous solutions of PBA-PAA-PBA were characterized using TEM and DLS. The results are presented and discussed below.

Acrylate-acrylic acid-acrylate copolymers could easily form micelles based on TEM results in solution. With hydrocarbon chain length increased than normal surfactant, results showed special structure with four hydrophilic groups. The micelle structure in water solution was shown in Figure 5. Due to four hydrophilic groups, hydrophobic groups occupied more space and easier to form micellar structures. These unique properties might also be due to the increase in hydrophobicity caused by the interaction between two hydrocarbon chains.

The fully extended length of the hydrocarbon chain I_c , which formed the part of hydrophilic group and hydrophobic core, could be calculated by Tanford's formula²²:

$$I_c = 0.154 + 0.127n \text{ (nm)} \quad (4)$$

In which n was the number of methylene groups for the hydrocarbon chain of the surfactant. For PBA-PAA-PBA

$$n = \frac{M_n}{m} (n_{AA} + n_{Acrylate}) \quad (5)$$

In which m was the quality of the copolymer. The I_c values were estimated to be 15.18 nm for PBA-PAA-PBA, which was consistent with the TEM results. Light scattering particle size analysis [Figure 5(B)] also showed that the average particle diameter is 33.79 nm.

These results indicated that the membranes in the micelles for PBA-PAA-PBA featured a large pore structure which is shown in Figure 5. This large pore structure is formed possibly due to the larger hydrocarbon chain in the polymeric gemini surfactant. Thus, the formation of this structure appeared to be related to the origins of certain effective performance of a surfactant, such as low CMC and surface tension in water.

CONCLUSIONS

PMA-PAA-PMA, PBA-PAA-PBA, PIA-PAA-PLA, PLA-PAA-PLA and PTA-PAA-PTA triblock copolymers with a narrow molecular weight distribution were successfully synthesized via RAFT polymerization in ethyl acetate. The designed and synthesized polymeric gemini surfactants were characterized by ¹H NMR spectroscopy, GPC in terms of their compositions, molecular weight and behavior at the air-water interface. The result showed that a narrow molecular weight distribution (PDI < 1.40) of acrylate-acrylic acid-acrylate copolymer via RAFT polymerization under mild reaction conditions could be achieved and a special micelle structure with large pore structure could be observed.

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