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Effects of subphase pH and temperature on the interfacial behavior of double hydrophilic diblock copolymer PDEGMA-*b*-PDIPAEMA

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Abstract

The aggregation behavior of two pH- and temperature-responsive diblock copolymers of poly[di-(ethylene glycol) methyl ether methacrylate]-*block*-poly[2-(diisopropylamino) ethyl methacrylate] (PDEGMA-b-PDIPAEMA) at the air/water interface and the structures of their Langmuir-Blodgett (LB) films were studied by the Langmuir monolayer technique and atomic force microscopy, respectively. At the air/water interface, PDEGMA-b-PDIPAEMA tends to form the core-shell-corona micellar structure composed of a PDIPAEMA main chain core, an amino ethyl ester shell, and a PDEGMA corona. Under acidic, neutral, and alkaline conditions, PDIPAEMA blocks are completely protonated, partially protonated, and completely non-protonated, respectively, and the protonated amino ethyl ester groups are immersed in water before monolayer compression, whereas PDEGMA coronas are adsorbed at the interface. At pH 3, 7, and 10, the limiting areas (A₀) for PDEGMA42%-PDIPAEMA58% (weight percents) and PDEGMA55%-PDIPAEMA45% are 8.2/10.2/14.0 and 6.7/8.3/8.4 nm², respectively. The A_0 values of the former copolymer are larger than those of the latter. This is because the shells in the former copolymer are denser due to the higher polymerization degree of PDIPAEMA blocks, providing greater steric hindrance for PDEGMA coronas and making the latter more extended at the interface. In contrast to other copolymer systems, the effect of temperature on the isotherms of PDEGMA-b-PDIPAEMA is less obvious.

KEYWORDS: Langmuir monolayer; LB film; double hydrophilic block copolymer; environmentally responsive polymer; subphase pH

1 INTRODUCTION

Due to their self-assembly properties, block copolymers have a wide range of application in many fields such as optics,¹⁻⁶ nanostructures,⁷⁻¹⁴ and composite materials.¹⁵⁻¹⁸ At the air/water interface, amphiphilic diblock copolymers can self-assemble into specific supramolecular ordered aggregates/micelles. Common amphiphilic diblock copolymer (PS-*b*-PEO),^{19–22} polystyrene-*block*-poly(ethylene oxide) systems such as (PS-*b*-PMMA),^{22,23} polystyrene-*block*-poly(methyl methacrylate) polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-P2VP)²⁴⁻²⁶, polystyrene-*block*-poly(acrylic acid) (PS-b-PAA)²⁷ and poly(n-butylacrylate)-b-poly(acrylic acid) (PnBA-b-PAA)^{28,29} have been widely studied. The aggregate structures are mainly affected by copolymer composition,^{19,25,30} spreading solvent type,^{24,25} and solution concentration.²⁷ With the increase of the content of hydrophobic blocks, the copolymers tend to form circular,¹⁹ rod,²⁵ and planar aggregates²⁵ at the air/water interface. Glagola et al. examined the interfacial aggregation behavior of PS-b-PEO and characterized the Langmuir-Blodgett (LB) films by atomic force microscopy (AFM).¹⁹ The experimental results showed that the copolymers can form circular and mixed aggregates when PEO contents were larger and lower than 20 wt%, respectively, which was affected by their spreading degree and inter-segment forces. Our group once studied the solvent effect on the interfacial behavior of PS-b-P2VP and found that the LB films prepared with non-selective solvents exhibited isolated circular micelles, whereas those with selective solvents were abundant, including circular micelles, rod aggregates, planar aggregates, and labyrinth pattern.²⁵ Besides, the effects of spreading solution concentration and surface pressure on the interfacial aggregation behavior of PS-*b*-PAA were examined by Wang's group.²⁷ They showed that a pseudo-plateau emerged in the Langmuir isotherm, which corresponded to a pancake-to-brush transition with the PAA chains gradually dissolving in the subphase. In the LB films, a variety of morphologies such as worm-like, porous structures and dots were observed.

In recent years, environmentally responsive polymers have received considerable attention in both polymer and colloidal science.^{31–34} In different stimulation environments, polymers form different nanostructures in aqueous solution due to the different interactions between the polymers and the solvents.^{35–39} The types of environmental stimuli can usually be divided into two major categories: chemical stimulation and physical stimulation. Chemical stimuli, such as pH, can alter the interactions between polymer chains or between chains and solvent at the molecular level. Physical stimuli such as temperature, light, electrical, and magnetic fields affect the thermodynamic and physical parameters of the system and alter the molecular interactions.³⁸ At present, some environmentally responsive block copolymers containing poly(N-isopropylacrylamide) (PNIPAM),^{40–42} poly[2-(dimethylamino)ethyl methacrylate] $(PDMAEMA)^{43-45}$ and poly[2-(diisopropylamino) ethyl methacrylate] (PDIPAEMA)^{38} were mainly studied. At the air/water interface, the aggregation behavior of environmentally responsive block copolymers was also influenced by copolymer type, subphase pH,^{26,46–48} and temperature.^{43,49–53} Our group investigated the effects of copolymer composition and subphase pH/temperature on the aggregation behavior of amphiphilic diblock copolymers poly[2-(dimethylamino)ethyl methacrylate]-*block*-poly(lauryl methacrylate) (PDMAEMA-b-PLMA) at the air/water interface.⁵³ We found that the surface pressure–molecular area (π –A) isotherms of the copolymers gradually moved to larger mean molecular area (mmA) with the increase of subphase pH, and most LB films showed isolated circular micelles. The detailed morphology of the aggregates depended on various interactions: hydration of PDMAEMA chains, electrostatic repulsion between protonated PDMAEMA chains, spatial repulsion between unprotonated PDMAEMA blocks and hydrophobic interactions between PLMA cores. On the other hand, these interactions should be dependent on copolymer composition and subphase pH/temperature. Under acidic conditions, however, the LB films of the predominantly hydrophobic PDMAEMA-b-PLMA prepared at low temperature exhibited worm-like aggregates. This was due to the weaker electrostatic repulsion between the immersed short PDMAEMA strands than the hydrophobic interactions of PLMA aggregates, and the neighboring PLMA cores spontaneously formed worm-like aggregates. Under neutral/alkaline conditions, the LB films prepared at high temperature showed different aggregate structures. This was due to the possibility that locally abundant short PDMAEMA blocks may be compressed into the space between large PLMA cores.

As far as we know, researchers concentrated on studies of double hydrophilic block copolymers (DHBCs) in solutions,^{54–56} whereas the interfacial behavior of these copolymers studied.49,52,54 rarely In the interfacial behavior of was our group, poly(N-isopropylacrylamide)-*block*-poly[oligo(ethylene glycol) acrylate] (PNIPAM-b-POEGA) was studied and a sunflower-like structure was proposed for the first time.⁴⁹ Its micellar structure was composed of a small PNIPAM backbone core, a short amide

shell, and several large POEGA petals, which was different from the typical core-corona structure in the amphiphilic diblock copolymer systems. In this work, the aggregation behavior of two pH- and temperature-responsive DHBCs of poly[di-(ethylene glycol) methyl methacrylate]-*block*-poly[2-(diisopropylamino) ether ethyl methacrylate] (PDEGMA-b-PDIPAEMA) at the air/water interface and the micelle structures of their Langmuir–Blodgett (LB) films were studied by the Langmuir monolayer technique and AFM, respectively. Langmuir monolayer technology can infer and understand the stacking mode of specific molecules in two-dimensional space, and its surface pressure-molecule area $(\pi - A)$ isotherms can also provide the average area occupied by each molecule and the compressibility of this monolayer. This technique is widely used to study the structure and properties of molecules at interfaces, such as surfactants, polymers, proteins, and lipids. AFM is a very convenient method to characterize the surface morphology, micro-structure, and possible defects present in polymeric films, ranging from micrometers to nanometers to molecular scale. Combining the monolayer isotherms and the AFM images of the LB films, it is possible to infer the aggregation mechanism of the copolymers at the air/water interface. PDEGMA is a temperature-sensitive hydrophilic polymer, and its lower critical solution temperature (LCST) is ~27 $^{\circ}C$,^{38,45,56} which shows hydrophilicity and weak hydrophilicity at lower and higher temperatures, respectively. Due to its good biocompatibility and the LCST that can be adjusted, PDEGMA is also considered as a new temperature-sensitive polymer to replace PNIPAM. PDIPAEMA is a double-responsive hydrophilic polymer containing tertiary amine functional groups with a pK_a of ~6.2 and its LCST is ~28 °C.³⁸ At pH 3, the amine

groups of PDIPAEMA accept protons and are fully protonated, whereas hydrophilic PDEGMA is less affected by solution pH. At pH 7 and 10, PDIPAEMA blocks are partially protonated and completely non-protonated, respectively. We study the effects of subphase pH and temperature on the aggregation behavior of PDEGMA-*b*-PDIPAEMA diblock copolymers at the air/water interface, which can enrich the available knowledge on systems of double hydrophilic polyelectrolytes. At the same time, the two types of blocks in this system are biocompatible. Exploring the interface behavior of such copolymers can provide practical guidance for their specific application in biomedical research, drug release and other fields, and also provide new ideas for the design of their nanostructures and the research of new materials in biomedical science.

2 EXPERIMENTAL SECTION

2.1 Materials and reagents

The two DHBCs of PDEGMA-*b*-PDIPAEMA used in the work were synthesized by the reversible addition–fragmentation chain transfer (RAFT) polymerization methodology using PDEGMA as the macro-CTA, 2,2'-azobis(isobutyronitrile) (AIBN) as initiator, and 1,4-dioxane as solvent.³⁸ The weight-average molecular weights (M_w), number-average molecular weights (M_n), and polydispersity indices (PDI) of the two block copolymers were determined by size exclusion chromatography (SEC), and their chemical compositions were determined by ¹H-NMR spectroscopy.³⁸ The molecular characteristics and chemical structure of the two copolymers are shown in Table 1 and Scheme 1, respectively. According to the M_w

of PDEGMA42%-PDIPAEMA58% and PDEGMA55%-PDIPAEMA45%, the degrees of polymerization (DP) of PDEGMA and PDIPAEMA blocks were calculated to be 19/23 and 19/14, respectively.

S 1	$M_{ m w}{}^{ m a}$	$M_{ m n}$		wt%	wt%
Samples	$(g.mol^{-1})$	$(g.mol^{-1})$	$M_{\rm W}/M_{\rm n}$	(PDEGMA) ^b	(PDIPAEMA) ^b
PDEGMA42%-PDIPAEMA58%	8500	7200	1.18	42	58
PDEGMA55%-PDIPAEMA45%	6500	5510	1 18	55	45

TABLE 1 Molecular characteristics of PDEGMA-b-PDIPAEMA copolymers.

^a by GPC in THF at 25 °C, ^b Calculated by ¹H-NMR.



PDEGMA PDIPAEMA

SCHEME 1 Chemical structure of PDEGMA-*b*-PDIPAEMA copolymers.

In the experiments, HPLC-grade chloroform was used to prepare 0.5 mg/mL PDEGMA-*b*-PDIPAEMA solution. Ultrapure water (pH 7, resistivity of 18.25 M Ω ·cm) was prepared with a purification system (Molecular 1810C, China). Analytical grade 98% H₂SO₄ and NaOH were used to prepare subphase solutions of pH 3 and 10, respectively.

2.2 Determination of isotherms and hysteresis curves

The π -A isotherms and hysteresis curves of PDEGMA-b-PDIPAEMA monolayers were obtained by using a KSV minitrough (Finland) with an effective area of $324 \times 75 \text{ mm}^2$. The experimental procedure was similar to that described in our previous papers.²⁶ The isotherms of the two copolymers were determined at different subphase temperatures (10, 20, and 30 °C) by using a circulator bath (TED-0510, China) and pHs (3, 7, and 10). The subphase conditions were selected based on the LCSTs (27 and 28 °C) of PDEGMA and PDIPAEMA blocks, and pK_a of PDIPAEMA (6.2).³⁸ Before starting the experiments, subphase temperature was first calibrated with a thermometer. A copolymer solution of 16–18 µL was uniformly dropped on the water surface, the initial surface pressures of the copolymer monolayers after spreading were between 0.2-0.3 mN/m. After 15 min, the solvent was completely evaporated, and PDEGMA-b-PDIPAEMA formed a uniform monolayer on the water surface. During the experiments, the monolayers were compressed by the movement of two barriers at 5 mm/min, and the isotherms were recorded.²⁹ To ensure the accuracy of the experiment, each isotherm was repeated at least twice with good reproducibility until they almost/completely overlapped. The hysteresis curves were determined at different pH values and at 20 °C. In a hysteresis experiment, the monolayer was compressed to $mmA = 4 mm^2$, and then the barriers were held for 30 s, and finally they returned to their initial positions at the same speed of 5 mm/min.

2.3 Preparation and characterization of LB films

The Langmuir monolayers of PDEGMA42%-PDIPAEMA58% and PDEGMA55%-PDIPAEMA45% were transferred to the silicon wafers to obtain their

corresponding LB films at different subphase pH values and at 20 °C. Before the transfer, the silicon wafers were cleaned and treated to be hydrophilic based on the modified RCA cleaning procedure given by our group.²⁶ The LB films under the initial conditions were first transferred by pulling the silicon wafer vertically from the subphase at 2 mm/min without barriers' movement. Then surface pressure was compressed to 5 (pH 3) or 10 mN/m (pH 7 and 10) and maintained for 20 min to ensure the stability of the Langmuir monolayer, and finally, the LB films were prepared by further pulling the silicon wafer at the same speed. The LB films' transfer ratios of the above two diblock copolymers were in the range of 1.31–3.16 and 1.67–2.82, respectively. To reveal the aggregation mechanism of the monolayers, the LB films were characterized using an AFM apparatus (AFM5100N, Hitachi, Japan) at room temperature. The Multi75Al monolithic silicon probes (Budget Sensors) had a spring constant of 3 N/m and the amplitude was ~1.00 V. The scanning speed was 1.0 Hz, and the scanning area was $0.5 \times 0.5 \text{ um}^2$ (resolution of $256 \times 256 \text{ dots}$). Each LB film was usually scanned two times to ensure good reproducibility and the average diameter of the micellar cores was measured by using the cross-section method on 8 cores.⁴⁹

3 RESULTS AND DISCUSSION

3.1 Subphase pH effect on isotherms

At the air/water interface, PDEGMA-*b*-PDIPAEMA tends to form the core-shell-corona micellar structure with a PDIPAEMA main chain core, an amino ethyl ester shell, and a PDEGMA corona, which is similar to the core-shell-petal structure in the DHBC type

PNIPAM-b-POEGA system studied in our group.⁴⁹ Figure 1 shows the π -A compression isotherms of PDEGMA-b-PDIPAEMA monolayers at different subphase pH values and at 20 °C. In Figure 1, the isotherms are of an expanded type and the initial surface pressures under different conditions are relatively low and remain almost unchanged till $mmA = 20 \text{ nm}^2$. Upon further compression, PDEGMA coronas contact each other, and surface pressure increases gradually. With the increase of subphase pH values, the π -A isotherms of the two diblock copolymers move towards larger mmA due to the increased stretching degrees of PDEGMA coronas, which is similar to the behavior of POEGA in our previous PNIPAM-b-POEGA system.⁴⁹ At pH 3, 7, and 10, the limiting areas (A₀) for PDEGMA42%-PDIPAEMA58% and PDEGMA55%-PDIPAEMA45% are 8.2/10.2/14.0 and 6.7/8.3/8.4 nm², respectively. The A_0 values were obtained by extrapolating the linear part (8-23 mN/m) of the isotherms to 0 mN/m. Under acidic conditions, the amino ethyl ester groups are fully protonated (localized positive charge on nitrogen atom) and already immersed in the subphase before compression, whereas PDEGMA coronas are adsorbed on the water surface. Under neutral and alkaline conditions, PDIPAEMA blocks are partially protonated and completely non-protonated, respectively. The non-protonated amino ethyl ester shells adsorb on the water surface. From the above data, the A_0 values of PDEGMA42%-PDIPAEMA58% are larger than those of PDEGMA55%-PDIPAEMA45%. This is because the shells in the former copolymer are denser due to the higher DP of PDIPAEMA blocks, providing greater steric hindrance for PDEGMA coronas and making the latter more extended at the interface. Furthermore, under alkaline conditions, the isotherm of PDEGMA42%-PDIPAEMA58% presents a turn at 22

mN/m due to the gradual immersion of PDEGMA coronas, which is different from the appearance of pseudo-plateaus in the PNIPAM-*b*-POEGA system under different pH conditions.⁴⁹



FIGURE 1 π -*A* isotherms of the monolayers of two PDEGMA-*b*-PDIPAEMA copolymers at different subphase pH values and at 20 °C.

3.2 Subphase pH effect on hysteresis curves

Figure 2 shows the hysteresis curves of the two PDEGMA-*b*-PDIPAEMAs at different subphase pH values and at 20 °C. Table 2 shows the ΔA_0 values of the isotherms shown in Figure 2. The hysteresis degrees can be indicated by $\Delta A_0 = A_0 - A_0$ ', where A_0 ' is the limiting area of the expansion isotherm. In Figure 2, different hysteresis degrees appear under different conditions. Compared to those of PDEGMA55%-PDIPAEMA45%, the ΔA_0 values of PDEGMA42%-PDIPAEMA58% at the same pH values are larger due to the significant shrinkage of the more stretched PDEGMA coronas upon compression. At pH 10, the hysteresis degree of PDEGMA42%-PDIPAEMA58% is the largest among the three pH conditions. Upon monolayer compression, PDEGMA coronas with the largest stretching degree are pressed into the subphase (corresponding to the turn in the isotherm) and are difficult to return to the interface upon monolayer expansion due to the hydrogen bonds between the ether oxygen groups and water molecules. However, the hysteresis degree of PDEGMA55%-PDIPAEMA45% at pH 7 is larger than that at pH 10 due to the partial immersion of PDEGMA blocks based on the smaller steric hindrance of the partially protonated shells. At pH 10, the amino ethyl ester groups are completely non-protonated, the π -A compression isotherm does not present a turn, which is different from the other copolymer. This indicates that PDEGMA coronas here are not pressed into the subphase, and they only contact and shrink upon monolayer compression. In our point of view, the hysteresis degrees mainly reflect the initial states of the DHBC-type PDEGMA-*b*-PDIPAEMA



FIGURE 2 Hysteresis curves of the two PDEGMA-*b*-PDIPAEMA copolymers at different subphase pH values and at 20 °C.

Subphase condition	PDEGMA42%-PDIPAEMA58%	PDEGMA55%-PDIPAEMA45%
рН 3	3.7	2.5
pH 7	4.1	3.4
рН 10	8.1	1.0

TABLE 2 ΔA_0 values (in nm²) of the isotherms shown in Figure 2.

3.3 Subphase temperature effect on isotherms

Figures 3 and 4 show the π -A isotherms of PDEGMA42%-PDIPAEMA58% and PDEGMA55%-PDIPAEMA45% monolayers at different subphase pH values and temperatures, respectively. The A_0 values in Figures 3 and 4 are given in Table 3. Under different pH conditions, the isotherms shown in Figures 3 and 4 exhibit almost similar trends and are less affected by subphase temperature. This is different from the large temperature effects on our previous amphiphilic block copolymers PDMAEMA-b-PLMA53 and DHBC-type PNIPAM-b-POEGA⁴⁹ due to the different copolymer types and probably to the smaller $M_{\rm n}$ values in the current systems, respectively. In most cases, the isotherms at 10 $^{\circ}{\rm C}$ move to the largest mmA, which is different from those at the far left side in our previous study.⁴⁹ This is because PDEGMA coronas do not shrink substantially at 10 °C, whereas they shrink more at 20 °C due to their enhanced molecular mobility (thermal motion). When subphase temperature (30 °C) is higher than the LCST (28 °C) of PDIPAEMA blocks, the isotherms slightly move to larger mmA due to the increased stretching degree of PDEGMA caused by the conformation change of PDIPAEMA. We believe the LCST behavior of PDEGMA blocks is less obvious and can be ignored at least in the temperature range we study. Under alkaline condition, the isotherm of PDEGMA42%-PDIPAEMA58% at 30 °C shows a more obvious turn (24 mN/m) than that at 20 °C due to larger mobility of PDEGMA blocks.



FIGURE 3 π -A isotherms of PDEGMA42%-PDIPAEMA58% monolayers at different subphase pH values and temperatures.



FIGURE 4 π -A isotherms of PDEGMA55%-PDIPAEMA45% monolayers at different subphase pH values and temperatures.

	PDEGMA42%-PDIPAEMA58%			PDEGMA55%-PDIPAEMA45%		
Subphase condition	10 °C	20 °C	30 °C	10 °C	20 °C	30 °C
рН 3	11.5	8.2	10.5	9.5	6.7	7.2
pH 7	11.5	10.2	11.7	8.5	8.3	8.5
pH 10	11.4	14.0	13.8	9.1	8.4	8.8

TABLE 3 A_0 values (in nm²) of the isotherms shown in Figures 3 and 4.

Under neutral conditions, the isotherms of PDEGMA55%-PDIPAEMA45% move to large mmA with the increase of temperature due to the less dense shells providing the smaller steric hindrance, which shows the relatively significant temperature effect on the stretching of PDEGMA coronas. With the increase of temperature, hydrogen bonding force decreases, and molecular mobility and stretching degree of PDEGMA coronas increase. Furthermore, the isotherm at 30 °C exhibits an obvious turn at 25 mN/m, corresponding to immersion of PDEGMA coronas.

3.4 Subphase condition effect on the LB films

It is usually assumed that the structure of the monolayers remains unchanged during the transfer process to a solid substrate to obtain the corresponding LB films. Figures 5 and 6 show the AFM height images of the LB films of PDEGMA42%-PDIPAEMA58% and PDEGMA55%-PDIPAEMA45% transferred at different subphase pH values and at 20 °C, respectively. The average diameters of the micellar cores in Figures 5 and 6 are listed in Table 4. All the LB films show isolated circular micelles with small cores (8–10 nm) due to the lack of strongly hydrophobic blocks⁴⁹ in PDEGMA-*b*-PDIPAEMA and the low DP of PDIPAEMA blocks. The yellow dots in the images are the micellar cores formed by the PDIPAEMA main chain part. PDEGMA coronas and amino ethyl ester shells cannot be observed in the AFM height images. Some large bright regions are impurities possibly introduced during the cutting

and cleaning of the silicon wafers, and the brown stripes are the background noise. It is noted that many cores are invisible and covered by the background noise, therefore it is difficult for us to give the relationships between micellar core diameters and the subphase conditions/copolymer compositions.



FIGURE 5 AFM height images of the LB films of PDEGMA42%-PDIPAEMA58% transferred from acidic (**a**,**d**), neutral (**b**,**e**), and alkaline subphases (**c**,**f**) at 20 °C. Transfer conditions are at initial positions (**a**–**c**), and 5 (**d**) and 10 mN/m (**e**,**f**). Two typical micellar cores in panel a are designated with black cycles. The insets given in $150 \times 150 \text{ nm}^2$ are zoomed from the large images.



FIGURE 6 AFM height images of the LB films of PDEGMA55%-PDIPAEMA45% transferred from acidic (**a,d**), neutral (**b,e**), and alkaline subphases (**c,f**) at 20 °C. Transfer conditions are at initial positions (**a**–**c**), and 5 (**d**) and 10 mN/m (**e,f**). The insets given in 150 \times 150 nm² are zoomed from the large images.

Panels	5a	5b	5c	5d	5e	5f
Diameter (nm)	9±2	9±1	7±1	9±1	11±1	9±1
Panels	ба	6b	6с	6d	6e	6f
Diameter (nm)	9±1	8±1	8±1	8±2	8±2	10±1

TABLE 4 Average diameters (nm) of micellar cores in Figures 5 and 6.

3.5 Possible micellar structure

Figure 7 shows the schematic diagram of the micelle conformations of the copolymers at different subphase pH values and at 20 °C. At the air/water interface, PDEGMA-*b*-PDIPAEMA copolymers form the core-shell-corona micellar structure composed

of PDIPAEMA main chain cores, amino ethyl ester shells, and PDEGMA coronas, which is similar to the core-shell-petal structure in our previous DHBC-type PNIPAM-*b*-POEGA system.⁴⁹ Under acidic conditions, the amino ethyl ester groups are fully protonated and already immersed into the subphase before monolayer compression. Under neutral and alkaline conditions, amino ethyl ester groups are partially protonated and completely non-protonated, respectively, and PDEGMA coronas are adsorbed on the water surface, and their stretching degrees increase with increasing subphase pH values. Upon compression, PDEGMA coronas contact each other, and PDEGMA coronas at pH 10 are immersed in water corresponding to the obvious turn in the above isotherm.



FIGURE 7 Schematic diagram of the micelle conformations of the copolymers at different subphase pH values and at 20 °C.

4 CONCLUSIONS

In this work, the effects of subphase pH and temperature on the interfacial behavior of two

DHBC-type PDEGMA-b-PDIPAEMA copolymers were studied. The

PDEGMA-b-PDIPAEMA copolymers tend to form the core-shell-corona micellar structure composed of PDIPAEMA main chain cores, amino ethyl ester shells, and PDEGMA coronas, which is similar to the core-shell-petal micellar structure in the DHBC type PNIPAM-b-POEGA system but different from the typical core-corona structures composed of hydrophobic block cores and hydrophilic block coronas in amphiphilic block copolymer systems. With the increase of subphase pH values, the π -A isotherms of the two diblock copolymers move towards larger mmA due to the increased stretching degrees of PDEGMA coronas. Under acidic conditions, the PDIPAEMA blocks are fully protonated and amino ethyl ester groups already immerse in the subphase before monolayer compression, PDEGMA coronas are adsorbed on the water surface. Under neutral and alkaline conditions, PDIPAEMA blocks are partially protonated and completely non-protonated, respectively. PDEGMA coronas are adsorbed on the water surface, which is pressed into the water phase upon monolayer compression under several pH and temperature conditions. At 10 °C, the isotherms appear at the largest mmA because PDEGMA coronas do not shrink substantially. At 20 °C, PDEGMA coronas shrink more due to the enhanced molecular mobility, and the isotherms move to the left. When subphase temperature (30 °C) is higher than the LCST (28 °C) of PDIPAEMA blocks, the isotherms slightly move to larger mmA due to the increased stretching degree of PDEGMA coronas as a response to the conformation change effect of PDIPAEMA. However, the temperature effect on PDEGMA coronas is less obvious, which keep their stretching state all the time. By exploring the responsive behavior of block copolymers under different conditions, we find that the interface behavior of PDEGMA-b-PDIPAEMA copolymers is some different from their solution behavior. It develops the research and application field of PDEGMA-*b*-PDIPAEMA, which can provide practical guidance for the specific application of biomedical research, drug release, and also can provide new ideas for the design of nanostructures and the study of new materials in biomedical science.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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