

Electric-Field-Induced Aggregation of Polymeric Micelles to Construct Secondary Assembly Films

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ABSTRACT: A new amphiphilic quaternary random ionomer (PIDHES) was used to construct self-assembly films. PIDHES was prepared by a selective ionization of quaternary random copolymer, poly(*N,N*-dimethyl amimethyl methacrylate-*co*-2-hydroxypropyl methacrylate-*co*-2-ethylhexyl acrylate-*co*-styrene) precursor, which was synthesized by free radical copolymerization of commercial hydrophilic monomers *N,N*-dimethyl amimethyl methacrylate and 2-hydroxypropyl methacrylate and hydrophobic monomers 2-ethylhexyl acrylate and styrene. PIDHES could self-assemble into polymer micelles in water, which underwent orientated deposition in the electric field and ultimately produced secondary assembly films. Scanning electron microscopy studies showed that the resultant PIDHES secondary assembly film was smooth and compact. Moreover, it was found that PIDHES micelles concentration and electric-field-induced time had a strong influence on the morphologies of the resultant secondary assembly film. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

KEYWORDS: amphiphilic; random copolymer; micelle; electric-field-induced; secondary assembly film

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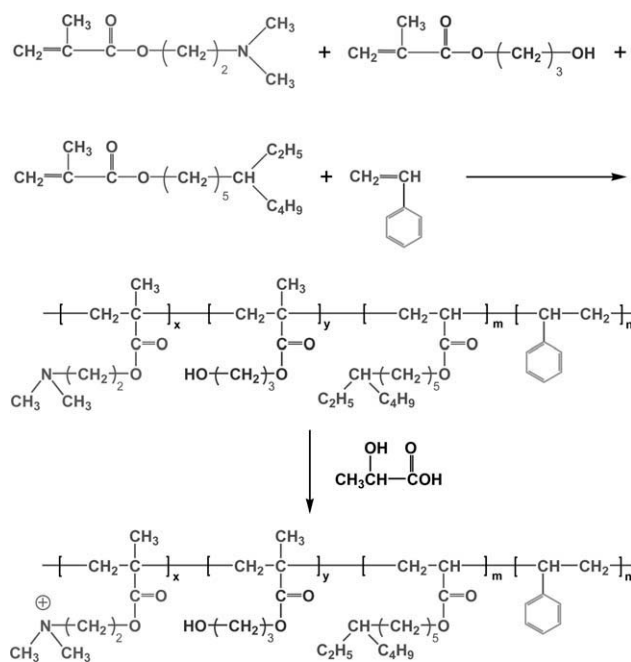
INTRODUCTION

Currently, functional self-assembly films continue to be a topical area of research because of its tremendous potentials in very diverse areas,¹ such as decorative coatings,^{2–4} (bio)sensors,^{5,6} light-emitting diodes,^{7,8} optical storage devices,¹ separation membranes.¹ Besides the layer-by-layer (LbL) assembly,^{9–12} different assembly techniques have been employed for self-assembly films formation, including covalent self-assembly,^{13,14} electric-field-induced assembly,¹⁵ etc. Moreover, various functional materials have been used as building blocks to construct the functional self-assembly films, such as nanoparticles,¹⁶ carbon nanotubes,^{17,18} enzymes,¹⁹ block copolymer micelles,^{20–23} and dendrimers.^{24,25}

Amphiphilic block copolymers are able to self-organize into core-shell micellar structures in selective solvent.^{26–40} Constructing functional self-assembly films from block polymer micelles is a long-term concern, because some water-insoluble polymers or organic molecules that are difficult to assemble with common method, can be assembled into multilayer thin films by incorporating into hydrophobic core of micelles.⁴¹ Kataoka and coworkers obtained a covalent-bonded layered

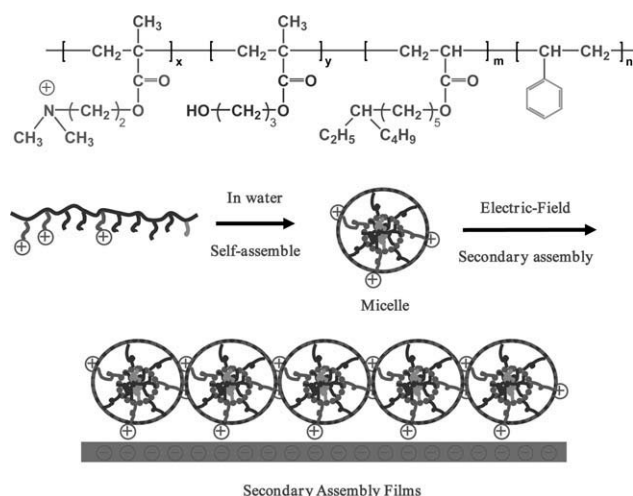
thin film by alternating deposition of poly(ethylene glycol)-*b*-poly(D,L-lactide) micelles and poly(allylamine).^{42,43} Because the hydrophobic core of micelles can incorporate drugs, the resultant functional self-assembly films could release drugs in a controlled manner; however, this method had limited applications because the procedure was extremely tedious, which included stabilization of the micelles by core polymerization, shell hydrolysis to make the surface of micelles bear reactive aldehyde groups, and the cross-linking between the micelles and poly(allylamine) to form a Schiff base between the layers. Following Kataoka's discoveries, Zhang and coworkers developed a kind of multilayer films using block copolymer micelles of poly(styrene-*b*-acrylic acid).²¹ These films had potential use as controlled assembly and release materials for some water-insoluble dyes. Subsequently, micelle/micelle multilayer films with dual optical properties were obtained employing protonated polystyrene-*block*-poly(4-vinylpyridine) (PS-*b*-P4VP) and anionic polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) block copolymer micelles.⁴⁴ However, the block copolymers mentioned earlier were synthesized by sequential anionic polymerization, which was limited by its strict conditions.

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Scheme 1. Synthesis route of amphiphilic quaternary random copolymer and ionomer.

Amphiphilic random copolymers were easy to synthesize and has more wide applications than amphiphilic block copolymers.^{45–50} Compared with block copolymers, the sequence and the distribution of hydrophilic and hydrophobic units are ill-defined or ill-regular. However, amphiphilic random copolymers could also self-assemble into a wide range of supramolecular structures such as spherical micelles and vesicles.^{51–55} In recent years, we have developed an “amphiphilic random copolymer” strategy for preparing micelles,^{56,57} in which amphiphilic random copolymer, such as poly(styrene-*co*-acrylic acid) or random copolymer MAF from methylacrylic acid, macro-monomer FA [$\text{CH}_2=\text{CHOOCH}_2\text{CH}_2(\text{OCOCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{OH}$],



Scheme 2. Schematic illustration of the preparation route to the secondary assembly films.

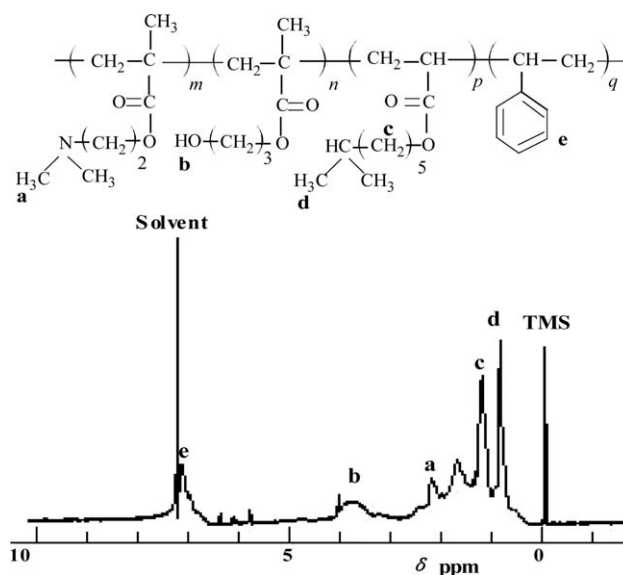


Figure 1. $^1\text{H-NMR}$ spectrum of PIDHES

and methyl methacrylate could self-assemble to ordered lacunose, bowl-shape or spherical micelles.

In this work, as shown in Scheme 1, an amphiphilic quaternary random ionomer bearing ionization quaternary ammonium groups (PIDHES), was prepared by the selective ionization of quaternary random copolymer, poly(*N,N*-dimethyl amimethyl methacrylate-*co*-2-hydroxypropyl methacrylate-*co*-2-ethylhexyl acrylate-*co*-styrene) (PDHES), which was synthesized by free radical copolymerization of commercial affordable hydrophilic monomers *N,N*-dimethyl amimethyl methacrylate (DMAM) and 2-hydroxypropyl methacrylate (HPMA) and hydrophobic monomers 2-ethylhexyl acrylate (EHA) and styrene (St) self-assembling of ionomer PIDHES into polymer micelles in water, followed by the orientated deposition of PIDHES micelles in the electric field, ultimately produced secondary assembly films (Scheme 2). Unlike functional self-assembly films from block copolymer micelles of PEG-*b*-PLA or PS-*b*-P4VP,^{42–44} the synthesis of Ionomer PIDHES, involved only free radical polymerizations, and the selective ionization of the tertiary amine groups was relatively simple and easy to deal with, which is extremely important for its future applications. Moreover, the

Table I. Summary of the Molecular Weights and Compositions of the Copolymers Prepared with Different Monomer Feed Ratio^a

Sample	DMAM/HPMA/EHA/St in copolymer (mol/mol)	M_n^b	M_w/M_n^b	T_g^c (°C)
PDHES6	6.6/58.4/21.8/13.2	40,000	1.3	14
PDHES8	8.6/57.2/21.4/12.8	52,000	1.8	17
PDHES10	10.3/55.8/21.1/12.8	34,000	1.4	20
PDHES15	15.0/55.0/17.2/12.8	64,000	1.4	28

^aThe polymerization was carried out at 90°C for 10 hr. Initiator AIBN: 1.0 wt % of the amount of monomers. ^bThe number-average molecular weight (M_n) and polydispersity index (M_w/M_n) were determined by size-exclusion chromatography, ^c T_g was determined by DSC.

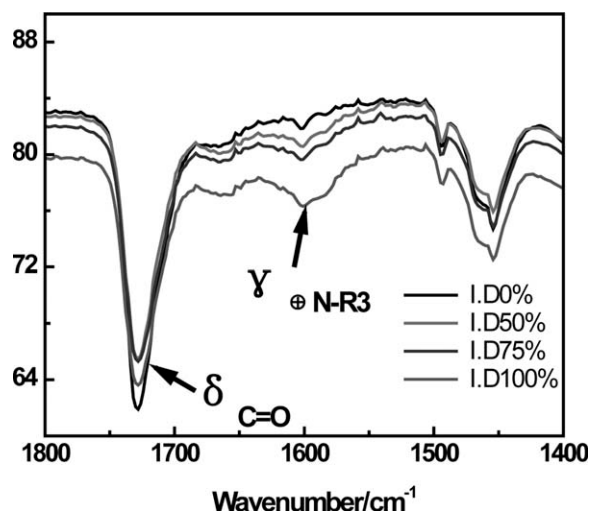


Figure 2. IR spectra of the ionomer PIDHES with different ionization degree.

resultant PIDHES secondary assembly film was smooth and compact, which would be useful in various fields, such as decorative coatings and (bio) sensors.

EXPERIMENTAL

Materials

α,α -Azo-bis-(isobutyronitrile) (AIBN) (Kishida >99%) was purified by recrystallization from methanol. DMAM, HPMA, and EHA were purified by basic aluminum oxide column. St was dried over CaH₂, and then distilled under reduced pressure before polymerization. All other reagents from Shanghai Chemical Reagent Factory were purified following standard procedures prior to use.

Measurements

¹H-NMR spectra were acquired on a Bruker Avance Digital 400 MHz NMR spectrometer in CDCl₃. The molecular weight and polydispersity of polymer were determined with a gel permeation chromatography (GPC, Agilent 1100) using DMF as the eluent (1.0 mL/min) at 35°C. The calibration curve was estab-

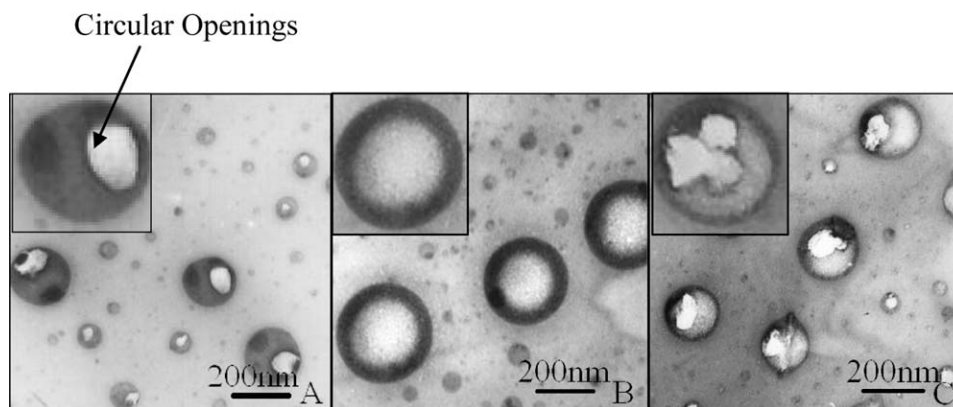


Figure 3. TEM images of the ionomer PIDHES6 micelles prepared in different selective solvents. Micelles concentration: 5.0×10^{-4} g/mL, ionization degree (ID) = 100%, selective solvent: (A) DMF; (B) 1,4-dioxane; (C) isopropanol/1-butanol (v/v = 2/1).

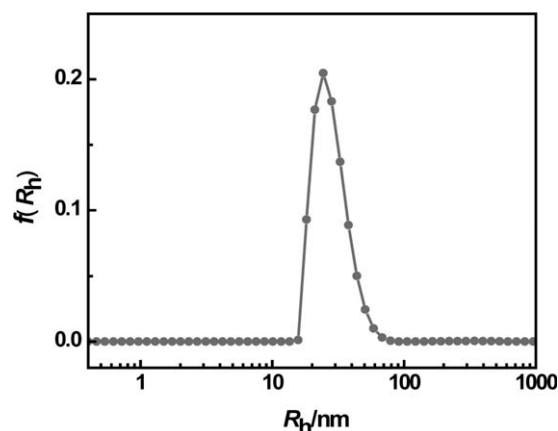


Figure 4. Hydrodynamic radius (R_h) of the ionomer PIDHES6 micelles; Micelles concentration: 5.0×10^{-4} g/mL, ionization degree (ID) = 100%, Selective solvent: DMF.

lished using a set of narrowly distributed PS as the standard. The hydrodynamic radius, R_h , of the nanoparticles was measured by laser light scattering (ALV500E, ALV Co., Germany). All dynamic laser light-scattering (DLS) measurements were performed at $\theta = 80^\circ$ and 25°C , and all samples were clarified through a $0.45\text{-}\mu\text{m}$ Teflon membrane filter (Chromatographic Specialties Inc.). Transmission electron microscopy (TEM) images were obtained with a Hitachi 7000A microscope operated at an acceleration voltage of 150 kV at a magnification of 100,000 times. Specimens were prepared by slow evaporation of a drop of approximately diluted solution deposited onto a collodion-coated copper mesh grid, followed by carbon sputtering or by OsO₄ staining.

Preparation of PDHES

PDHES was synthesized by free radical copolymerization of *N,N*-dimethyl amimethyl methacrylate, 2-hydroxypropyl methacrylate, EHA, and St. In a typical experiment, monomers, initiator AIBN (1.0 wt % of the amount of monomers), and mixed solvents isopropanol/1-butanol (v/v = 2/1) were introduced into a previously dried Schlenk flask filled with nitrogen, and the mixture was degassed three times by freeze-pump-thaw cycles.

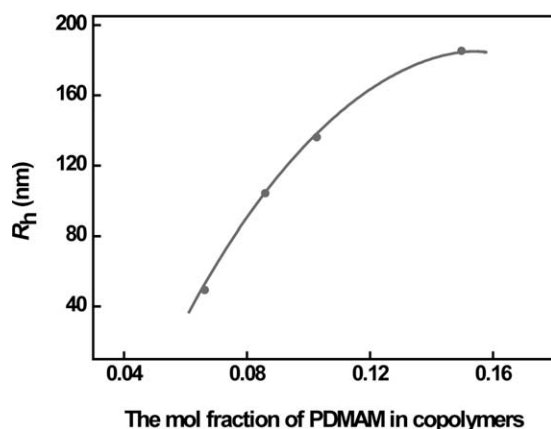


Figure 5. Effect of the hydrodynamic radius (R_h) of micelles on the content of PDAM units in copolymer; Micelles concentration: 5.0×10^{-4} g/mL, ionization degree (ID) = 75%, selective solvent: DMF.

The polymerization was performed under nitrogen flow at 90°C for 10 hr. The polymers formed were then dissolved in acetone and recovered by precipitation into excess of 1 : 4 (v/v) methanol/water and dried *in vacuo* at room temperature. The molecular weight distribution (M_w/M_n) of PDHES was determined by GPC and the ratios of each unit in the resulting copolymer were determined by $^1\text{H-NMR}$ analysis. Four PDHES samples with different ratio of each unit were prepared.

Preparation of PIDHES

In a typical experiment, PDHES random copolymer was dissolved in DMF in a round-bottom flask. To the solution was then added lactic acid (1.0 equiv in comparison with DMAM units), and the reaction mixture was stirred for 80 min. The resulting polymers were then dissolved in acetone and recovered by precipitation into excess of 1 : 4 (v/v) methanol/water and dried *in vacuo* at room temperature. By controlling the amount of lactic acid, ionomer PIDHES with different ionization degree can be obtained.

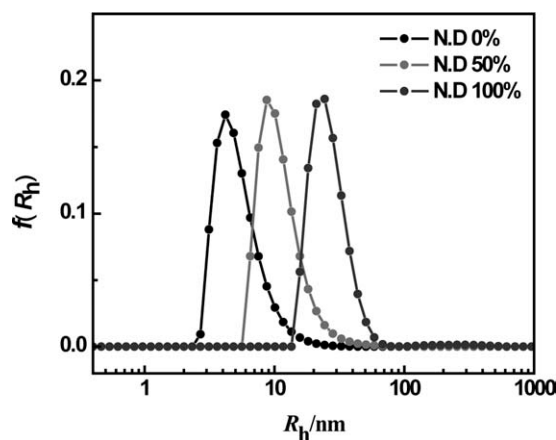


Figure 6. Hydrodynamic radius (R_h) of the micelles from ionomer PIDHES6 with different ionization degree (I.D.); Micelles concentration: 5.0×10^{-4} g/mL, Selective solvent: DMF.

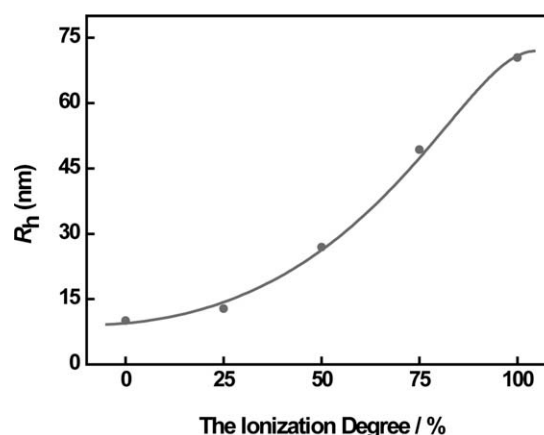


Figure 7. Effect of the different ionization degree (ID) of the hydrodynamic radius (R_h) of the ionomer PIDHES6 micelles; Micelles concentration: 5.0×10^{-4} g/mL, Selective solvent: DMF.

Formation of Micelles

Ionomer PIDHES (0.05 g) was dissolved in 100 mL of DMF, followed by filtration of the solution through a 0.45-mm Teflon membrane filter (Chromatographic Specialties, Inc.). The micelles were formed by the addition of the resulting DMF solution into water at a rate of 1 dropper per 60 s with continuous stirring. The micelle solution was stirred for 24 hr and then dialyzed in water using a cellulose dialyzer tube.

Electric-Field-Induced Self-Assembly of PIDHES Micelles

Copper foil, serving as cathode, was immersed into the PIDHES micelles solution (0.5 mg mL^{-1}) for 30 s under 50 V DC voltage. After the evaporation of the water, transparent secondary assembly films with a thickness of 5–15 μm were obtained.

RESULTS AND DISCUSSION

Synthesis of Quaternary Random Ionomer

A series of quaternary random copolymer PDHES with different contents of PDAM units (PDHES6, PDHES8, PDHES10, and PDHES15) were synthesized by a conventional radical copolymerization of commercial hydrophilic monomers DMAM and HPMA and hydrophobic monomers EHA and St using AIBN as initiator. The compositions and molecular weight distributions of PDHES random copolymers were determined by $^1\text{H-NMR}$ (Figure 1) and GPC (Table I). The M_n of the four copolymers was between 34,000 and 64,000 g/mol. The glass-transition temperatures (T_g) of the copolymers PDHES6, PDHES8, PDHES10 were $\sim 17^\circ\text{C}$. However, T_g of PDHES15 was up to 28°C ; the reduction in the contents of EHA units of PDHES15 may be responsible for its increase in T_g .

After the selective ionization of the tertiary amine groups of the PDAM unit by lactic acid, amphiphilic random ionomer PIDHES was obtained (Scheme 1). The ionization of the tertiary amine groups was confirmed by the appearance of the quaternary ammonium IR characteristics peaks at 1610 cm^{-1} (Figure 2). By controlling the amount of lactic acid, ionomer PIDHES with different ionization degree could be obtained. The ionization degree was calculated by the integration of the

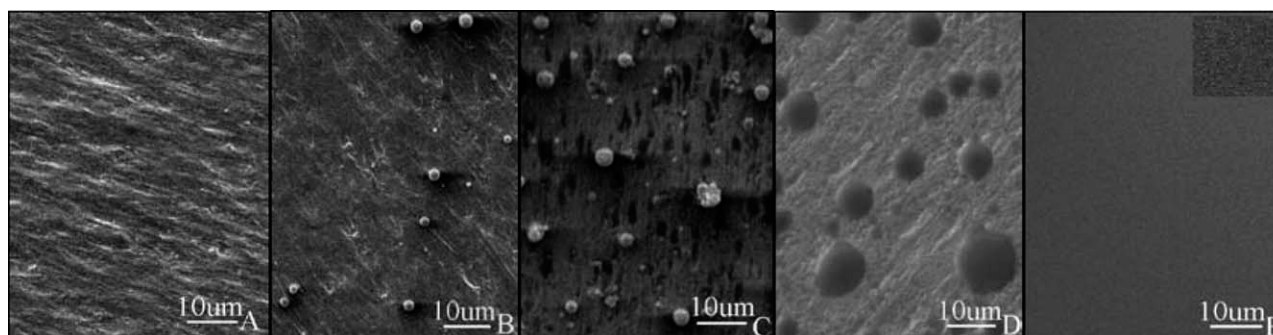


Figure 8. SEM images of the secondary assembly film from ionomer PIDHES6 micelles; ionization degree (ID) = 100%. (A) Copper foil; (B) electricity induction time: $t = 10\text{ s}$, $C = 1 \times 10^{-5}\text{ g/mL}$; (C) $t = 60\text{ s}$, $C = 1 \times 10^{-5}\text{ g/mL}$; (D) $t = 10\text{ s}$, $C = 1 \times 10^{-3}\text{ g/mL}$; (E) $t = 30\text{ s}$, $C = 1 \times 10^{-2}\text{ g/mL}$.

$\oplus\text{NR}_3$ characteristics peaks and $\text{C}=\text{O}$ characteristics peaks at 1725 cm^{-1} in IR spectrum (Figure 2).

Micelles Formation of PIDHES

The micelles were then prepared by the self-assembly of ionomer PIDHES in selective solvents (Scheme 2). Polymer micelles were formed by first dissolving PIDHES in a good solvent (DMF, 1,4-dioxane or isopropanol/1-butanol ($v/v = 2/1$)) and then gradually adding water as a nonsolvent for PSt and PEHA unit. The resultant micelle solution was stirred for 24 hr and then dialyzed in water using a cellulose dialyzer tube. Micelle morphologies were directly observed using a transmission electron microscope (TEM). The TEM images of the micelles prepared in different selective solvents were shown in Figure 3. When the selective solvent was DMF, the random ionomer formed mainly regular bowl-shaped aggregates [Figure 3(A)]. The diameters of the bowls were in the range of 60–200 nm, and the diameters of the circular openings were between 30 and 90 nm. While the selective solvent was 1,4-dioxane, hollow polymer spheres were clearly observed [Figure 3(B)]. The diameters of the hollow spheres were between 280 and 350 nm, and the cavity size is in the range of 220–250 nm. Spheres with irregular crevasse [Figure 3(C)] on the wall were obtained, using isopropanol/1-butanol ($v/v = 2/1$) as selective solvent. It is really very difficult to explain why the morphology different in various selected solvents in content. Perhaps different solvents have different interactions with copolymers, consequently, resulted in different morphology. The average size and size distribution of micelles could also be determined from DLS measurement. The R_h was 71 nm for bowl-shaped micelles from the DLS method (Figure 4), which was consistent with the TEM results [Figure 3(A)]. The hydrodynamic radius distribution of the micelles was unimodal (Figure 4), indicating the formation of the expected monodispersed nano-scale micelles. Ionomer PIDHES with different composition and ratio of the hydrophobic and hydrophilic segments were used to prepare micelles of different dimensions. The dependence of micelle size on the composition of PDMAM units was investigated by DLS. In all cases, size polydispersity ($\mu_2/\langle\Gamma\rangle^2$) was found to be in the range 0.08–0.16, indicating the particles showed relatively narrow size distributions. The particle size varied considerably, depending on the mol fraction of the PDMAM units, and ranged from 49

to 185 nm (Figure 5). This observation was reasonable because an increase in the PDMAM unit content could induce a relative increase in the hydrophilic interaction of copolymers, which would certainly make the aggregate looser. A similar phenomenon was also observed in the other micelle systems.^{29,57}

The effects of ionization degree of copolymers on self-assembly behavior were also investigated. As shown in Figures 6 and 7, micelles from copolymer PDHES without ionization had a very small R_h (10 nm), and the R_h increased with increasing ionization degree, and the largest R_h (70 nm) was obtained for totally ionization sample. The increase in R_h of the resultant micelles with the increasing ionization degree of copolymer, was attributed to the increase of the hydrophilicity of the copolymer chains, which made the hydrophilic segments more extended. This would obviously lead to the swelling of the particles and thus the increase of R_h .

Electric-Field-Induced Self-Assembly of PIDHES Micelles

Secondary assembly films were then fabricated by orientated deposition of PIDHES micelles with positive charges on a copper foil surface in the electric field. Figure 8 shows SEM images of the secondary assembly process of PIDHES micelles. As shown in Figure 8, with lower concentration micelles ($C = 1 \times 10^{-5}\text{ g/mL}$), spherical particles with a narrow size distribution [Figure 8(B)] were obtained during secondary assembly. Increasing the electric-field-induced time, more micelles would deposit on copper foil, leading to secondary assembly spherical particles with larger size [Figure 8(C)]. When the micelles concentration reached $1 \times 10^{-3}\text{ g/mL}$, disc-shaped particles with the size in the range of 6–10 μm [Figure 8(D)] were obtained. Further increasing the micelles concentration to $1 \times 10^{-2}\text{ g/mL}$ would lead to a smooth and compact secondary assembly film [Figure 8(E)] after depositing for 30 s. Since the resultant assembly film was insulated, a further extension of deposition time may cause side reactions, leading to unsmooth assembly film. This indicated that both the micelles concentration and electric-field-induced time were important for the formation of good assembly film. Thus, amphiphilic quaternary random ionomers PIDHES micelles could form smooth and compact secondary assembly film by electric-field induction under proper conditions.

CONCLUSIONS

A convenient and cheap way to construct smooth and compact secondary assembly films was developed by electric-field-induced aggregation of amphiphilic random copolymers micelles. Amphiphilic quaternary random ionomer (PIDHES) was prepared by a selective ionization of quaternary random copolymer, PDHES precursor, which was synthesized by free radical copolymerization of commercial hydrophilic monomers DMAM and HPMA and hydrophobic monomers EHA and St. Scanning electron microscopy studies showed that the resultant PIDHES secondary assembly film was smooth and compact. Moreover, it was found that PIDHES micelles concentration and electric-field-induced time had a strong influence on the morphologies of the resultant secondary assembly film. The resultant films would be useful in various fields, such as decorative coatings and (bio)sensors.

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