Multiple stimuli-responsive amphiphilic block copolymers of poly(methacrylic acid) (PMAA) and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) were used as emulsifiers to prepare two-way CO₂ stimuli-responsive poly(methyl methacrylate) (PMMA) latex particles via aqueous emulsion polymerization. The polymerization at pH 2 and 50 °C produced mainly PDMAEMA-surfaced PMMA latex particles, whereas the polymerization at pH 12 and 50 °C produced mainly PMAA-surfaced particles. Both types of latex particles appeared to precipitate at higher pH values from the emulsifier of a longer PDMAEMA block length. The direction from precipitation to dispersion for PDMAEMA-surfaced particles or from dispersion to precipitation for PMAA-surfaced particles in response to CO₂ bubbling of the pH 12 dispersion of particles depended on the PDMAEMA block length. Together, this study reveals that—by tuning the PDMAEMA block length in PMAA-b-PDMAEMA used as an emulsifier and polymerization at pH 2 or 12—PMMA latex particles can exhibit two-way CO₂ responsiveness between dispersion and precipitation. Thus, due to their simple preparation and unique dual pH and CO₂ responsiveness, these newly developed PMAA-b-PDMAEMA emulsifiers provide a highly efficient approach for the development of smart PMMA latex nanoparticles with desirable multifunctional properties.

**ABSTRACT:** Multiple stimuli-responsive amphiphilic block copolymers of poly(methacrylic acid) (PMAA) and poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) were used as emulsifiers to prepare two-way CO₂ stimuli-responsive poly(methyl methacrylate) (PMMA) latex particles via aqueous emulsion polymerization. The polymerization at pH 2 and 50 °C produced mainly PDMAEMA-surfaced PMMA latex particles, whereas the polymerization at pH 12 and 50 °C produced mainly PMAA-surfaced particles. Both types of latex particles appeared to precipitate at higher pH values from the emulsifier of a longer PDMAEMA block length. The direction from precipitation to dispersion for PDMAEMA-surfaced particles or from dispersion to precipitation for PMAA-surfaced particles in response to CO₂ bubbling of the pH 12 dispersion of particles depended on the PDMAEMA block length. Together, this study reveals that—by tuning the PDMAEMA block length in PMAA-b-PDMAEMA used as an emulsifier and polymerization at pH 2 or 12—PMMA latex particles can exhibit two-way CO₂ responsiveness between dispersion and precipitation. Thus, due to their simple preparation and unique dual pH and CO₂ responsiveness, these newly developed PMAA-b-PDMAEMA emulsifiers provide a highly efficient approach for the development of smart PMMA latex nanoparticles with desirable multifunctional properties.

**INTRODUCTION**

Multiple stimuli-responsive polymer materials have received significant attention in numerous applications.1−3 Temperature and pH are the most well-characterized stimuli for polymeric materials in aqueous media,4−6 and gas stimuli have recently received increased attention.7−10 CO₂ has been reported as an environmentally friendly stimulus due to its nonflammability, nontoxicity, and ease of removal.11−13 CO₂ can function as a stimulus to transform neutral and hydrophobic tertiary amine groups or amide groups in water into charged and hydrophilic ammonium bicarbonate or amidinium bicarbonate, respectively.14−16 Such transformations can be subsequently reversed by removing the CO₂ by simply purging with an inert gas such as nitrogen, argon, or air.14 Poly(dimethylaminoethyl methacrylate) (PDMAEMA) is one example of a tertiary amine-containing polymer.16 In addition to CO₂ stimuli-responsive tertiary amine and amide functional groups that transform from neutral to cationic in aqueous solution, the COOH group of carboxylic acid can function as a CO₂ stimuli-responsive functional group that transforms from anionic to neutral.19 At high solution pH values, CO₂ transforms the dissociated carboxylates (anionic organic bases) of carboxylic acids from a more hydrophilic form (CO₂⁻) to the less hydrophilic COOH form. The direction of transformation for the neutral forms of bases (e.g., amines and amides) is the opposite of the negatively charged forms of bases (e.g., carboxylates). Poly(methacrylic acid) (PMAA) functions as an anionic organic base in aqueous solution at high pH values. At high solution pH values, the relatively hydrophobic COOH groups of PMAA dissociate into hydrophilic carboxylate anions (COO⁻). The carboxylate anions can reversibly associate with protons to form relatively hydrophobic COOH groups on bubbling CO₂. As a result, at high solution pH values, water-soluble PMAA can be converted into a water-insoluble polymer by bubbling CO₂ to lower the pH. The direction of the CO₂-induced transformation between hydrophilicity and hydrophobicity for PMAA is opposite of that for PDMAEMA; PMAA transforms from water-soluble to -insoluble, whereas PDMAEMA transforms from water-insoluble to -soluble on CO₂ bubbling. Thus, the PMAA and PDMAEMA segments present in the polymer structure play a critical role in self-assembly capability and result in diverse nanostructures with unique chemical and physical properties in aqueous solution.20

Diblock copolymers of PMAA and PDMAEMA can exhibit two-way CO₂ stimuli responsiveness, and the amphiphilicity of PMAA-b-PDMAEMA diblock copolymers can be tuned by bubbling CO₂. While we recently demonstrated that the amphiphilicity of PMAA-b-PDMAEMA diblock copolymers of fixed PMAA block lengths and four different PDMAEMA block lengths can be switched on/off in a two-way manner by CO₂ bubbling, which enabled the block copolymers to function as emulsifiers for oil-in-water emulsification.21 The opposite CO₂-
induced switches in the hydrophilicity of PMAA and PDMAEMA enabled the preparation of versatile, multifunctional block copolymer emulsifiers. Previous studies demonstrated that poly(N,N-dimethylaminoethyl methacrylate)-b-poly(N-isopropyl acrylamide) (PDMAEMA-b-PNIPAM) exhibits temperature- and pH-triggered amphiphilicity under specific temperature and solution pH conditions.22,23 In aqueous solution, this block copolymer can self-assemble into micelles to emulsify oil in water by bubbling CO2, and the emulsification can be reversed by subsequent N2 bubbling.24,25 This block copolymer in aqueous solution was further demonstrated as an emulsifier for emulsion polymerization of methyl methacrylate (MMA) to prepare PDMAEMA-coated poly(methyl methacrylate) (PMMA) latex particles that exhibit one-way CO2-responsive dispersion.26 The resulting latexes contain tertiary amines on their surface and can be easily destabilized by removing the CO2 by bubbling an inert gas and/or increasing the temperature to switch the hydrophilic ammonium bicarbonate surface to a hydrophobic neutral amine surface, without the need for traditional approaches such as adding salts, strong acids, or strong alkalis. The aggregation and redispersion of the resulting latex particles can be reversibly controlled by alternating between N2 and CO2 bubbling.27–29 Therefore, the potential applications of CO2/N2 as a stimulus to create an ecofriendly programmable “green emulsion” with multifunctional amphiphilic characteristics are highly desirable.

In this study, we demonstrate the preparation of two-way CO2 stimuli-responsive dispersion of PMMA latex particles via emulsion polymerization using two-way CO2 stimuli-responsive PMAA-b-PDMAEMA diblock copolymers as emulsifiers at pH 2 and 50 °C or pH 12 and 50 °C (Scheme 1). Emulsion polymerization at pH 2 and 50 °C gave rise to PMMA latex particles with strongly hydrophilic PDMAEMA chains on their surface, whereas polymerization at pH 12 and 50 °C gave rise to PMMA latex particles with strongly hydrophobic PMAA chains on their surface. The opposite directions of the CO2-induced on/off switch in the hydrophilicity of PMAA and PDMAEMA enabled the preparation of a two-way CO2 stimuli-responsive dispersion of PMMA latex particles. Overall, this work provides an example of a dual-responsive diblock copolymer with reversibly controllable gas- and pH-switchable amphiphilic characteristics that can be used to manipulate the reversibility of emulsification/demulsification in response to pH changes and CO2/N2 bubbling. Therefore, these newly developed PMAA-b-PDMAEMA diblock copolymers hold significant potential for the development of smart emulsion nanoparticles with controllable structures, sensitive pH and CO2/N2 responsiveness, and reversible switching of emulsions between the aqueous and organic phases.

Scheme 1. Preparation of Positively and Negatively Charged PMAA-b-PDMAEMA and Emulsion Polymerization of MMA Using PMAA-b-PDMAEMA as an Emulsifier at pH 2 or pH 12

Emulsion Polymerization of MMA Using PMAA-b-PDMAEMA as an Emulsifier at pH 2 or pH 12 in N2. 1H nuclear magnetic resonance (NMR) was performed on all samples at 25 °C to explore the structural characteristics of the PMMA latex particles. 1H NMR spectra were generated in dimethyl sulfoxide (DMSO)-d6 (Figure S1) to determine the compositions of the constituent PMMA and block copolymer within PMMA latex particles prepared by emulsion polymerization. By integrating the appropriate peak area ratios in Figure S1, the weight fractions of the block copolymer and PMMA in the latex particles were determined to be about 5 and 95 wt %, respectively, for all four types of latex particles. These compositions are almost consistent with our reaction design and stoichiometry (Table S1). Furthermore, Fourier transform infrared (FTIR) spectra barely indicated the characteristic peaks of PMAA at 3400 cm−1 for CH3 stretching in N−CH3 and the characteristic broad peak of PMMA at 1740cm−1. The finding that both of these peaks barely appeared in the FTIR spectra of PMMA latex particles (Figures S2 and S3) indicated that a very small quantity of the block copolymer emulsifier was present on the surface of the PMMA latex particles. The NMR and FTIR analyses indicated that PMMA latex particles were successfully synthesized using a small amount of PMAA-b-PDMAEMA surfactant. In addition, all types of PMMA latex particles exhibited high molecular weights, as shown in the gel permeation chromatography (GPC) data in Figure S4 and Table S2. The thermal properties of PMAA-b-PDMAEMA/PMMA latex particles were further explored by differential scanning calorimetry (DSC) at temperatures ranging from −20 to 170 °C. Figure S5 shows the DSC curves of pure PMMA and PMMA latex particles prepared by emulsion polymerization at pH 2 and pH 12. Clear glass transition temperatures (Tg) were observed for all samples and are tabulated in Table S3. The Tg of pure PMMA was 106 °C compared to around 118–129 °C (Table S3) for the PMMA latex particles. The single Tg increased for each particle sample (Figure S5), suggesting PMAA-b-PDMAEMA and PMMA are compatible within PMMA latex particles; this observation can probably be attributed to increased interaction between the PMMA and PMAA-b-PDMAEMA segments.30

Scanning Electron Microscopy (SEM) Images of PMAA-b-PDMAEMA/PMMA Nanoparticles. To investigate
the particle size distribution and morphology of the resulting latex particles, the PMMA latex particle dispersions prepared by emulsion polymerization of MMA in water at pH 2 and 50 °C using the four PMAA-b-PDMAEMA block copolymers as emulsifiers were dripped on a glass plate and dried in an unheated vacuum oven and the particles were assessed by SEM. For SEM measurements, the dispersion prepared at pH 2 was also adjusted to pH 12 or until precipitation occurred. As indicated by the SEM images in Figure 1, the dried particles from the as-synthesized dispersion (pH 2) were spherical, clearly separated from each other, and about 100–150 nm in diameter for all four copolymers as emulsifiers. Thus, all four copolymers at pH 2 could all self-assemble into micelles and serve as stable emulsifiers, with the hydrophilic PDMAEMA block likely outside the micelles and the relatively hydrophobic PMAA block likely inside the micelles. A longer PDMAEMA block length seemed to lead to larger particles (at pH 2). The particles from the pH 12 dispersions and pH 2 dispersions appeared similar for all emulsifiers, except for the PMAA50-b-PDMAEMA7 emulsifier as the dried particles from the pH 12 dispersion appeared to stick to each other due to strong ionic interactions between sodium carboxylate arising from the addition of NaOH. This suggests that PMAA chains were present on the surface of these particles; the particles could not precipitate at such low pH values if only PDMAEMA chains were present on the surface.

The PMMA latex particle dispersions prepared by emulsion polymerization of MMA at pH 12 and 50 °C using the four PMAA-b-PDMAEMA block copolymers as emulsifiers were dripped onto a glass plate and dried in an unheated vacuum oven, and the particle morphology was investigated by SEM. The as-prepared pH 12 dispersions were also adjusted to pH 2 or until precipitation occurred. As shown in Figure 2, the morphologies and sizes of the dried particles from the as-synthesized dispersion (pH 2) were spherical, clearly separated from each other, and about 100–150 nm in diameter for all four copolymers as emulsifiers. Thus, all four copolymers at pH 2 could all self-assemble into micelles and serve as stable emulsifiers, with the hydrophilic PDMAEMA block likely outside the micelles and the relatively hydrophobic PMAA block likely inside the micelles. A longer PDMAEMA block length seemed to lead to larger particles (at pH 2). The particles from the pH 12 dispersions and pH 2 dispersions appeared similar for all emulsifiers, except for the PMAA50-b-PDMAEMA7 emulsifier as the dried particles from the pH 12 dispersion appeared to stick to each other due to strong ionic interactions between sodium carboxylate arising from the addition of NaOH. This suggests that PMAA was present on the surface of the particles as the short PDMAEMA block length in the outer layer of the formed micelles barely prevented PMAA from exposure to the surface of the as-synthesized particles.

The pH at which the dispersions precipitated increased with the PDMAEMA block length, indicating that hydrophilic PDMAEMA was mostly located in the outer layer of the formed micelles (and thus the as-synthesized particles) since the water solubility of PDMAEMA decreases as the solution pH increases. For the PMAAS0-b-PDMAEMA7 and PMAAS0-b-PDMAEMA24 emulsifiers with low PDMAEMA block lengths, precipitation occurred at pH 5 and 6, respectively. This suggests that the PMAA chains were present on the surface of these particles; the particles could not precipitate at such low pH values if only PDMAEMA chains were present on the surface.
The stability of the micelles would depend on the constituent block lengths. As shown in Figure 2, the PMMA50-b-PDMAEMA7 emulsifier did not result in clearly separated spherical particles, whereas the PMMA50-b-PDMAEMA24 emulsifier appeared to give clearly separated spherical particles with diameters of about 200 nm. This suggests that PMMA50-b-PDMAEMA7 did not form stable micelles, whereas PMMA50-b-PDMAEMA24 did form stable micelles. Particle size decreased as the PDMAEMA block length increased, indicating that longer PDMAEMA block lengths could lead to a higher degree of entanglement and greater contraction of the micelles in size.

The dried particles from the pH 2 and pH 12 dispersions appeared similar, which can be attributed to the fixed PMMA block length of the four copolymers prepared in this study. In addition, the pH at which the dispersions precipitated increased with the PDMAEMA block length. This finding suggests that—in addition to the PMMA chains—parts of the PDMAEMA chains were present on the surface of the particles and the portion of PDMAEMA exposed increased with the PDMAEMA block length. The precipitation pH would be the same for all four latex samples when only the PMMA chains were present on the surface of the particles.

**pH Responsiveness of PMMA Latex Particle Dispersions.** The PMMA latex particle dispersions prepared by emulsion polymerization of MMA at pH 2 and 50 °C using the four PMMA-b-PDMAEMA block copolymers as emulsifiers were pH-responsive (Figure 3). Under these conditions (pH 2 and 50 °C), PMMA-b-PDMAEMA micelles would have hydrophilic PDMAEMA in the outer layer, whereas relatively hydrophobic PMMA is retained within the inner layer of micelles. Therefore, the prepared PMMA latex particles would have hydrophilic PDMAEMA on the surface of the particles and relatively hydrophobic PMMA embedded within the hydrophobic PMMA. These PMMA latex particles could disperse in aqueous solutions at low pH values and aggregated at high pH values as PDMAEMA is water-soluble at low pH values and water-insoluble at high pH values. However, as shown in Figure 3, the latex particles appeared to be homogeneously dispersed at both low and high pH values. This indicates the PMMA chains were not entirely embedded in PMMA; regions of the PMMA chains must be exposed on the surface of the PMMA latex particles to allow the particles to disperse well in water at both low and high pH values. The precipitation pH values ranged from pH 5 to 10 depending on the PDMAEMA block length; a longer PDMAEMA block length seemed to restrict exposure of the PMMA chains to a greater extent, leading to precipitation at higher pH values (Figure 3).

PMMA-b-PDMAEMA micelles at solution pH 12 and 50 °C would possess hydrophilic PMMA blocks in their outer layer and the hydrophobic PDMAEMA blocks would stay in the inner layer. Therefore, PMMA latex particles prepared under these conditions would have hydrophilic PMMA chains on their surface and hydrophobic PDMAEMA chains embedded in the hydrophobic PMMA particles. These PMMA latex particles would aggregate in aqueous solutions at low pH but would stably disperse in aqueous solutions at high pH. However, as shown in Figure 4, the particles appeared to be homogeneously dispersed at both low and high pH values, indicating that the hydrophobic PDMAEMA chains were not entirely embedded in PMMA. Part of the PDMAEMA chains must be exposed on the surface to allow the PMMA latex particles to disperse well in water at low and high pH values. The precipitation pH values appeared to depend on the PDMAEMA block length.
seemed to lead to greater exposure of the PDMAEMA chains and precipitation at a higher pH (Figure 4). The PMAA50-b-PDMAEMA7 block copolymer with the lowest PDMAEMA block length led to the aggregation of the latex particles at pH values as low as pH 2 due to the low density of PDMAEMA chains on the surface of these particles.

**CO₂ Responsiveness of PMMA Latex Particle Dispersions.** The PMMA latex particle dispersions prepared by emulsion polymerization of MMA at pH 2 and 50 °C using the four PMAA-b-PDMAEMA block copolymers as emulsifiers were also CO₂-responsive (Figure 5). The PDMAEMA in the other three dispersions remained homogeneous. Upon subsequent N₂ bubbling at 40 °C for 30 min, the pH went back up to pH 8.1—8.5. The PMAA50-b-PDMAEMA7/PMMA dispersion remained homogeneous, whereas the PMAA50-b-PDMAEMA24/PMMA aggregation redispersed and both the PMAA50-b-PDMAEMA72/PMMA and PMAA50-b-PDMAEMA266/PMMA dispersions clearly aggregated. As indicated in Figure 3, the precipitation pH values were 5, 6–8, and 8–10 for the PMAA50-b-PDMAEMA7/PMMA, PMAA50-b-PDMAEMA24/PMMA, PMAA50-b-PDMAEMA72/PMMA, and PMAA50-b-PDMAEMA266/PMMA dispersions, respectively. The precipitation pH values are determined by the amount of PDMAEMA and PMAA on the surface of the latex particles, as previously discussed in Figure 3. Since alternate CO₂ and N₂ bubbling into the pH 12 dispersions changed the pH values to 5.4 and 8.5, respectively, the accompanying response between dispersion and aggregation only occurred for dispersions with sufficient amounts of the copolymers on the surface of the latex particles. For instance, the pH 12 PMAA50-b-PDMAEMA7/PMMA dispersion did not exhibit CO₂- and N₂-responsive aggregation and dispersion as CO₂ and N₂ bubbling changed the pH values to 5.5 and 8.1, respectively (Figure 3). The latex particles could disperse in water at both of these pH values, as the exposed PMAA shielded the short PDMAEMA7 block length in the outer layer of the particles (which precipitate at pH 5; Figure 3). Since it was difficult to bring down the pH to 5 by CO₂ bubbling, the PMAA50-b-PDMAEMA7 block copolymer with a very short PDMAEMA block length could not be used as an emulsifier to prepare CO₂-responsive PMMA latex particles. Therefore, the block lengths have to be controlled properly to obtain CO₂-switchable dispersions of PMMA latex particles when using PMAA-b-PDMAEMA block copolymers as emulsifiers.

The PMMA latex particle dispersions prepared by emulsion polymerization of MMA at pH 2 and 50 °C using the four PMAA-b-PDMAEMA block copolymers as emulsifiers were also CO₂-responsive (Figure 6). PMAA in PMAA-b-PDMAEMA micelles at pH 12 and 50 °C was hydrophilic and located in the outer layer, while the relatively hydrophobic PDMAEMA stayed in the inner layer. PMMA latex particles prepared under these conditions have hydrophilic PMAA on their surface, while relatively hydrophobic PDMAEMA is embedded in hydrophobic PMMA. As shown in Figure 6, the four types of PMMA latex particles all dispersed well in water at pH 12 and also, unexpectedly, at pH 2. This can be explained by partial exposure of PDMAEMA on the PMMA-rich surface of the particles so that as-synthesized PMMA latex particles could disperse in water at pH 2 (see the previous discussion on pH responsiveness; Figure 4).

Upon bubbling CO₂ for 5 min into the pH 12 dispersions, the pH went down to about 5.4–5.5. The PMAA50-b-PDMAEMA7/PMMA and PMAA50-b-PDMAEMA24/PMMA dispersions clearly aggregated, whereas the other two dispersions remained homogeneous. Upon subsequent N₂ bubbling at 40 °C for 30 min, the pH increased to 8.1–8.4. The PMAA50-b-PDMAEMA7/PMMA and PMAA50-b-PDMAEMA24/PMMA aggregations redispersed in water, whereas the two other dispersions aggregated. As shown in Figure 4, the precipitation pH values were 2–6, 4–5, 6–8, and 8–10 for the PMAA50-b-PDMAEMA7/PMMA, PMAA50-b-PDMAEMA24/PMMA, and PMAA50-b-PDMAEMA266/PMMA dispersions, respectively. The precipitation pH values are determined by the
amount of PDMAEMA and PMAA on the surface of the latex particles (as discussed previously for Figure 4). Since alternate CO$_2$ and N$_2$ bubbling into the pH 12 dispersions changes the pH values to about 5.4 and 8.4, respectively, the accompanying responsiveness between dispersion and aggregation only occurred for dispersions with a sufficient amount of copolymer on the surface of the latex particles. PMAA50-b-PDMAEMA7/PDMAEMA and PMAA50-b-PDMAEMA24/PDMAEMA appeared to aggregate on bubbling CO$_2$ and redispense on bubbling N$_2$, as CO$_2$ and N$_2$ bubbling changed the pH to 5.5 and 8.1 (Figure 6), allowing the latex particles to, respectively, aggregate and disperse in water (Figure 4). This can be explained by an insufficient amount of PDMAEMA chains on the surface of particles due to the short PDMAEMA block length in the copolymer emulsifier. The PMAA50-b-PDMAEMA72/PDMAEMA and PMAA50-b-PDMAEMA266/PDMAEMA dispersions remained homogeneous on bubbling CO$_2$ and aggregated on subsequent N$_2$ bubbling, as CO$_2$ and N$_2$ bubbling changed the pH to 5.4 and 8.4 (Figure 6), allowing the latex particles to respectively disperse and aggregate in water (Figure 4). Therefore, CO$_2$-switchable dispersion of PMMA latex particles prepared using the PMAA-b-PDMAEMA block copolymer as emulsifiers at pH 12 and 50 °C could also be controlled by the block length. Collectively, these observations demonstrate that these newly developed PMAA-b-PDMAEMA/PDMAEMA nanoparticles undergo reversible CO$_2$/N$_2$-switchable aggregation/redispersion under various pH conditions. Furthermore, the macroscopic amphiphilic characteristics of the copolymers can be easily controlled by tuning the ratio of PMAA and PDMAEMA block lengths.

**CONCLUSIONS**

PMAA-b-PDMAEMA copolymers of four different PDMAEMA block lengths (in which the PMAA block length was fixed at an average of 50 repeat units and the PDMAEMA block length varied from 7 to 266 repeat units) were synthesized by controlled/living reversible addition fragmentation chain transfer (RAFT) polymerization. The copolymers were used as emulsifiers at only 0.5 wt % and successfully fabricated nanosized PMMA latex particles via emulsion polymerization. The polymerization at pH 2 and 50 °C gave rise to mainly PDMAEMA-surfaced PMMA latex particles, whereas polymerization at pH 12 and 50 °C gave rise mainly PMAA-surfaced particles. Both types of latex particles precipitated at specific pH values depending on the PDMAEMA block length, with longer PDMAEMA block length leading to precipitation at higher pH values. Upon bubbling CO$_2$ into the pH 12 dispersion of particles, the pH reduced to about 5.4; upon subsequent N$_2$ bubbling, the pH returned to about 8.5. The direction from precipitation to dispersion for PDMAEMA-surfaced particles or from dispersion to precipitation for PMAA-surfaced particles in response to CO$_2$ bubbling depended on the PDMAEMA block length. Thus, PMAA-b-PDMAEMA copolymers could act as effective dual pH/CO$_2$-responsive emulsifiers for the development of PMMA latex nanoparticles that exhibit two-way CO$_2$-responsiveness between dispersion and precipitation.

**EXPERIMENTAL SECTION**

**Materials.** Methyl methacrylate (MMA, 99%; Showa) was purified by distillation at reduced pressure. Azobisisobutyronitrile (AIBN, Sigma-Aldrich) was recrystallized from methanol. The preparation and characterization of PtBuMA-b-PDMAEMA block copolymers of fixed PtBuMA block lengths and four different PDMAEMA block lengths and hydrolysis of the PtBuMA block to obtain four PMAA-b-PDMAEMA block copolymers (PMAA50-b-PDMAEMA7, PMAA50-b-PDMAEMA24, PMAA50-b-PDMAEMA72, and PMAA50-b-PDMAEMA266) were conducted as previously described.

**Emulsion Polymerization of MMA Using PMAA-b-PDMAEMA as an Emulsifier at pH 2 under N$_2$.** Emulsion polymerization of MMA was conducted in a four-necked 500 mL flask equipped with mechanical stirring and a condenser. PMAA-b-PDMAEMA (0.25 g) was added to 50 mL of deionized water in the flask, and the aqueous solution was adjusted to pH 2 using HCl and heated to 50 °C under N$_2$ bubbling to dissolve the PDMAEMA block. AIBN (0.2 g, 1.25 × 10$^{-3}$ mol) dissolved in MMA (5 g, 0.05 mol) was injected through the septum into the flask reactor to initiate emulsion polymerization of MMA at 50 °C with stirring at 200 rpm for 3 h under N$_2$ bubbling. At pH 2 and 50 °C under N$_2$, the PDMAEMA block is protonated to become hydrophilic and water-soluble, while the PMAA block has a low degree of acid dissociation, undergoes strong hydrogen bonding between COOH pairs, and has low water solubility. Thus, PMAA-b-PDMAEMA can be used as an emulsifier at pH 2 to form micelles in water, with the PMAA block toward the core and the PDMAEMA block in the shell. Emulsion polymerization of MMA initiated by AIBN in the presence of PMAA-b-

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![Figure 6. Photos of dispersions of 1 wt % (a) PMAA50-b-PDMAEMA7/PDMAEMA, (b) PMAA50-b-PDMAEMA24/PDMAEMA, (c) PMAA50-b-PDMAEMA72/PDMAEMA, and (d) PMAA50-b-PDMAEMA266/PDMAEMA prepared by emulsion polymerization of MMA using the four PMAA-b-PDMAEMA block copolymers as emulsifiers at pH 12. The resulting PMMA nanoparticle dispersions had pH values of 12 and were adjusted to pH 2. The pH 12 dispersions were bubbled with CO$_2$ for 5 min, followed by bubbling N$_2$ at 40 °C for 30 min. Photos were taken 4 h after each pH adjustment and CO$_2$/N$_2$ bubbling. The pH values shown below the photos were obtained immediately after each CO$_2$ or N$_2$ bubbling.](https://dx.doi.org/10.1021/acsomega.9b03319)
PDMAEMA at pH 2 and 50 °C under N₂ is illustrated in Scheme 1. The synthesized PMAA-b-PDMAEMA/PMMA latex or dispersion was centrifuged, the top portion of the clear solution was decanted, and the settled nanoparticles were added to 10 mL of deionized (DI) water and centrifuged again. The same procedure was repeated for a third time to obtain the white nanoparticle dispersion.

Emulsion Polymerization of MMA Using PMAA-b-PDMAEMA as an Emulsifier at pH 12 under N₂. This emulsion polymerization was prepared as described above, and the environmental pH was altered from 2 to 12. At pH 12 under N₂ at 50 °C, the PDMAEMA block is hydrophobic and water-insoluble, while the PMAA block has a high degree of acid dissociation to form hydrophilic COO⁻ anions and is water-soluble. The PMAA-b-PDMAEMA can be thus used as an emulsifier at pH 12 to form micelles in water, with the PDMAEMA block toward the core and the PMAA block in the shell.

Characterizations. Proton nuclear magnetic resonance (¹H NMR; JNM-ECS600R spectrometer; JOEL, Japan) at 600 MHz was used to quantitatively characterize the compositions of PMAA-b-PDMAEMA/PMMA nanoparticles in DMSO-d₆ solvent. Fourier transform infrared (FTIR, Spectrum Two; PerkinElmer) spectrometry was used to qualitatively characterize the PMAA-b-PDMAEMA/PMMA nanoparticles by casting from the tetrahydrofuran (THF) solutions onto KBr; spectra were measured at room temperature at a resolution of 2 cm⁻¹ and sensitivity of 16 scans. The molecular weights and polydispersity indices (PDI) of the PMAA-b-PDMAEMA/PMMA nanoparticles were determined using a gel permeation chromatography (GPC) system equipped with a series of two columns (PLgel 10 um Mixed-B; Polymer Laboratories) and a refractive index detector. Dimethylformamide (DMF) containing 20 mM LiBr was the eluent at a flow rate of 0.6 mL/min at 35 °C. The glass transition temperatures (T_g) of the PMMA nanoparticles were measured by differential scanning calorimetry (DSC; Q100; TA Instruments). The samples were initially heated (20 °C/min) to 180 °C and cooled (10 °C/min) to −50 °C and then heated at 20 °C/min to 180 °C to record T_g. Scanning electron microscopy (SEM; Hitachi) was used to examine the morphology of the PMMA nanoparticles prepared by emulsion polymerization. For PMAA-b-PDMAEMA/PMMA synthesized at pH 2, the pH of the nanoparticle dispersion was first adjusted from pristine pH 2 to pH 12 or until precipitation occurred. For PMAA-b-PDMAEMA/PMMA synthesized at pH 12, the pH was first from 12 to 2 or until precipitation occurred. The particle dispersions were dripped onto a glass plate and dried in an unheated vacuum oven before SEM.

pH Responsiveness of PMMA Nanoparticle Dispersions. Dispersions in water of 1 wt % PMAA-b-PDMAEMA/PMMA nanoparticles synthesized at pH 12 or 2 were adjusted to pH 12, 10, 8, 6, 5, 4, or 2 using aqueous HCl and NaOH. The phase changes (dispersion/aggregation) induced by changing pH at 25 °C were recorded using a digital camera. Photos were taken 8 h after each pH change.

CO₂ Responsiveness of PMMA Nanoparticle Dispersions. Dispersions in water of 1 wt % PMAA-b-PDMAEMA/PMMA nanoparticles synthesized at pH 2 and 12 were adjusted to pH 2 or 12 to investigate phase changes (dispersion or aggregation) in response to CO₂ bubbling. For the synthesis at pH 12, the appearance of aggregation after bubbling CO₂ for 5 min at 25 °C was recorded using a digital camera for the pH 12 PMAA-b-PDMAEMA/PMMA nanoparticle dispersion. After CO₂ bubbling, the solutions were bubbled with N₂ for 30 min at 40 °C and redispersion was recorded. For synthesis at pH 2, the disappearance of aggregation after bubbling CO₂ for 5 min at 25 °C was recorded using a digital camera for the pH 2 PMAA-b-PDMAEMA/PMMA nanoparticle dispersion. After CO₂ bubbling, the solutions were bubbled with N₂ for 30 min at 40 °C and aggregation recovery was recorded. Photos were taken 4 h after each gas bubbling; bubbling flow rates were controlled at 20 mL/min.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.9b03319.

¹H NMR and FTIR spectra; GPC and DSC curves; and weight fraction of PMAA-b-PDMAEMA (PDF)

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Author Contributions

Y.-C.Y. carried out all experiments. Y.-T.S. and C.-C.C. devised the project, designed the research, and edited the manuscript. All authors discussed the results and provided constructive comments to the final manuscript.

**Notes**

The authors declare no competing financial interest.

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