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Emulsifier-free poly[2-(diethylamino)ethyl methacrylate] microgels with cationic quaternary ammonium monomers

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ABSTRACT: Although poly[2-(diethylamino)ethyl methacrylate] (PDEA) microgels are biocompatible and show potential in drug delivery, little research exists with respect to their preparation. Therefore, emulsifier-free PDEA microgels were synthesized in the presence of cationic ammonium salts of 2-(dimethylamino)ethyl methacrylate (DMA) that were quaternized with 1-bromohexadecane, 1-bromooctadecane, 1-bromopentane, or benzyl chloride. These served as both comonomers and polymerizable surfactants, providing colloidal stability to the DEA droplets during polymerization. The stability of the microgel particles in different pH values between 4 and 11 was investigated by turbidity–wavelength measurements. The benzyl group containing monomer was the most stabilizing. The pH-responsive behavior of the microgels in dilute aqueous solution was examined with respect to the amount of DEA, amount of copolymer, type of copolymer, and water content. Most of the microgels remain colloidally stable up to a pH of 9.0, while particles are less than 300 nm in size at pH 8.0. The isoelectric points of the microgels are higher than 8.5 in most cases. In fact, this value exceeds 12.0 by modifying the amount of copolymer. © 2015 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2016**, *133*, 43196.

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INTRODUCTION

Stimuli-responsive microgels are lightly cross-linked latex particles that swell in response to external stimuli such as temperature, magnetic fields, and pH.[1–3] Their potential applications, especially in biotechnology[3–9] and pharmaceutical science,[10–15] make them very attractive for investigation. Particularly, significant research has reported the synthesis and use of temperature-responsive poly(*N*-isopropylacrylamide) microgels in drug delivery systems.[13,16–20] Meanwhile, other biocompatible microgels take advantage of their ability to change colloidal properties in response to shifts in physiological pH.[1,3,21–26]

Poly[2-(diethylamino)ethyl methacrylate] (PDEA) is a well-known, weakly acidic polymer characterized by a pK_a of about 7.3 and a tertiary amine group that is protonated in acidic medium.[27] This biocompatible polymer, as well as many others based on 2-(diethylamino)ethyl methacrylate (DEA), has been reported in the literature.[1,14,27–30] Comprehensive studies since the 1990s have focused on the preparation of PDEA and the properties of aqueous solutions of derived water-soluble polymers and block copolymers.[27,29–32] However, there are a limited number of studies on pH-responsive PDEA microgels.

PDEA microgels have been prepared mostly by emulsion polymerization, effected in the presence of various stabilizers.[1,33–35] In particular, Armes and co-workers used reactive macromonomer stabilizers to prepare a new class of sterically stabilized pH-responsive PDEA microgels.[1] More recently, pH-responsive amphoteric core–shell microgel particles were prepared in a two-step process. The cores in this case were comprised of cross-linked PDEA or poly(methacrylic acid) (PMAA), surrounded by a cross-linked PMAA or PDEA shell, respectively, with anionic and polymerizable stabilizers applied in the first and second steps, respectively.[35]

Emulsifier-free emulsion polymerization is one of the most convenient methods by which to produce monodisperse polymer particles with clean surfaces, an important feature if such particles are to be used in certain applications.[36] In this case, colloidal stability is achieved by employing ionizable initiators, or else by adding a hydrophilic comonomer during polymerization,[37–40] which has the added benefit of functionalizing the particles; most recently, sodium methacrylate has been applied in this way.[40] However, other strategies have also been employed, including, for example, where Guo *et al.*[39] used anionic biomacromolecule alginic acid. In addition, Bradley *et al.*[41]

Additional Supporting Information may be found in the online version of this article.

Table I. Synthesis Conditions and Physical Properties of the Synthesized Microgels[a]

Code	Water (mL)	DEA (mL)	QDMA (mM)	Diameter (nm)[b]	IEP
PDEA-1	50	1.2	13	56	10.8
PDEA-2	50	2.4	13	405	9.41
PDEA-3	50	4.8	13	[c]	[c]
PDEA-4	50	2.4	0	375	7.72
PDEA-5	50	2.4	6.5	425	8.69
PDEA-6	50	2.4	19.5	175	10.6
PDEA-7	50	2.4	26	145	>12.0
PDEA-8	50	2.4	13[d]	305	8.88
PDEA-9	50	2.4	13[e]	275	8.63
PDEA-10	50	2.4	13[f]	270	8.88
PDEA-11	75	2.4	13	84	9.46
PDEA-12	100	2.4	13	46	10.8
PDEA-13	150	2.4	13	53	9.58

[a] QDMA was DMA(C_{16}); EGDMA = 24 μL.
[b] Hydrodynamic diameters were measured at pH 8.0.
[c] Unstable particles resulting in coagulum.
[d,e]and [f] were DMA(C_8), DMA(C_5), and DMA(Bz), respectively.

copolymerized DEA with *t*-butyl methacrylate, then hydrolyzed the *t*-butyl moieties with acid to yield polyampholyte PDEA/PMAA microgels. Alternatively, the use of functionalized, polymerizable surfactants provides an easy way to elicit colloidal stability and increase functionality.[42,43]

Herein we report the emulsifier-free synthesis of PDEA microgels, prepared in the presence of polymerizable quaternary ammonium monomers, based on 2-(dimethylamino)ethyl methacrylate (DMA), that acted as both comonomers and surfactants. To our knowledge, such a species has never before been employed in the synthesis of responsive microgels. These quaternary ammonium ions (QDMA) contained *n*-hexadecyl, *n*-octyl, *n*-pentyl, and benzyl moieties, added through reaction with the corresponding halogenated hydrocarbons. The effects of several features on particle size and isoelectric points (IEPs) were studied, including the amount of DEA, the substituent's on the QDMA, the ratio of *n*-hexadecyl groups present, and the monomer/water ratio.

Incorporation of these cationic monomers into PDEA microgels may improve functionality in certain cases, especially for antimicrobial applications.

EXPERIMENTAL

Materials and Methods

DEA (Aldrich), DMA (Merck), and ethylene glycol dimethacrylate (EGDMA, Merck) were purified by passing them through basic alumina columns before use. The quaternization agents 1-bromohexadecane (Merck), 1-bromooctane (Merck), 1-bromopentane (Aldrich), and benzyl chloride (Merck) were used as received. Potassium persulfate (Merck) was of analytical grade. The remaining reagents and solvents were purchased from Aldrich and Merck. Distilled water was used in all experiments.

^{1}H NMR and ^{13}C NMR spectra were recorded on an Agilent 400 MHz Premium Compact+ AR in deuterium oxide (D_2O). Microgel particle sizes and distributions were measured by dynamic light scattering using a Malvern Zetasizer Nano ZS, equipped with a Red-He/Ne laser operating at 633 nm. The same instrument was used to measure zeta potentials at different pH values, this time with a Malvern MPT-2 autotitrator. All measurements were carried out in dilute aqueous dispersions. The morphologies of the microgel particles were investigated by using scanning electron microscope (SEM, Carl Zeiss ULTRA Plus). The samples were dried on carbon disks and coated with a thin layer of gold. A Beckman Coulter Avanti J-30I ultracentrifuge was used to precipitate the particles. Turbidimetric studies of microgel dispersions were carried out by using Shimadzu UV 2450 PC spectrophotometer at 500 nm as a function of solution pH. The solid content of the dispersion was 0.1% (w/w).

Turbidity–wavelength measurements were also performed to investigate the colloidal stability of the microgel dispersions following the procedure described elsewhere.[44,45] The absorbance of the dispersions containing 0.1% (w/w) solid particles and 10^{-5} M NaCl at a certain pH was measured over the range 400–625 nm. Measurements were repeated for each pH value ranges from 4 to 11. For a certain pH, the stability parameter, *n*, was calculated from the slopes of the plots log(absorbance) versus log(wavelength) which yields a straight line. The equation is given below:

$$n = \frac{-(d \log A)}{(d \log \lambda)}$$

QDMA Synthesis

QDMAs were prepared via quaternization of the tertiary amine moieties in DMA with an alkyl or aryl halide, according to a procedure previously established in the literature.[46] DMA (5 g, 31.8 mmol) was mixed with either the alkyl halides (15.9 mmol)

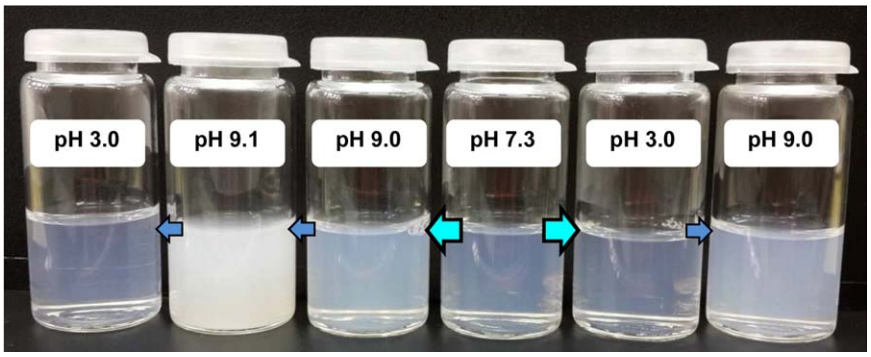

Figure 1. Images of PDEA-11 at pH values of 3.0, 7.3, 9.0 (bluish transparent microgel), and 9.1 (latex). The solution pH was changed from the initial pH value 7.3 to 3.0 (bluish transparent microgel form) and 9.1 (latex form). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

without any solvent or with benzyl chloride (31.8 mmol) and 20 mL of dichloromethane. After a small amount of hydroquinone was added, the mixture was stirred for 12 h at 50°C. The white solid precipitate was purified by washing it with dry diethyl ether for three times in order to remove unreacted material, after which it was recrystallized in acetone. The resulting white needle crystals were dried under vacuum for 48 h at room temperature. The QDMAs are identified as DMA(C_{16}), DMA(C_8), DMA(C_5), and DMA(Bz) for those produced using 1-bromohexadecane, 1-bromooctane, 1-bromopentane, and benzyl chloride, respectively; resulting yields were measured at 79%, 70%, 82%, and 95%, respectively. These monomers were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy (Supporting Information Figures S1 and S2).

Preparation of PDEA Microgels

The PDEA microgels were synthesized through a conventional emulsifier-free emulsion polymerization[47,48] in the presence of the synthesized QDMAs. Typically, polymerization was carried out in a 100 mL three-necked flask equipped with a condenser and a gas inlet. First, 50 mL of water were added into the flask, stirred, and purged with nitrogen for 30 min. Then, DMA(C_{16}) (0.3 g) was added, followed by a mixture of DEA (2.21 g) and EGDMA (0.025 g). The polymerization was initiated with the addition of potassium persulfate (1% of total monomer, w/w) and the flask was heated up to 70°C. The stirring was kept constant at 500 rpm over the 24 h polymerization, which was completed under nitrogen. After the addition of the initiator, the mixture changed from bluish-transparent to opaque, before finally settling on a milky dispersion. The amounts of monomer and initiator used in the experiments are listed in Table I, along with particle sizes and IEPs.

The obtained microgel particles were purified after polymerization through ultracentrifugation at 15,000 rpm for 15 min and then by washing with 50 mL of water. This cleaning procedure was repeated three times. Finally, the microgel particles were redispersed in deionized water.

RESULTS AND DISCUSSION

General Characteristics

All microgels in Table I, except for PDEA-3 which was aggregated, gave milky white dispersions. Overall, all the samples were effectively stable under the conditions tested, even up to a pH of 9.0.

The colloidal behavior of the various microgels is illustrated in Figure 1, using an aqueous dispersion of PDEA-11 as an example. The mixture was initially bluish-transparent at pH 7.3 due to swelling of the microgel. Surprisingly, this color did not change as the pH increased up to 9.0, even though the PDEA homopolymer is insoluble above pH 7.3[27] as a result of deprotonation of the tertiary amine group; in fact, the polymer was still structured as a microgel. It seems as though the incorporation of DMA(C_{16}) increased the pH microgel transition. Once the pH was increased above 9.0, the particles took on a non-solvated latex form and the solution became turbid. This transition was fully reversible. It is noteworthy that the EGDMA cross-linker did not cause any precipitation during the microgel-to-latex deswelling transition, as opposed to previous reports.[1]

Most of the microgel particles described in Table I were smaller than 300 nm in size at pH 8.0. However, the hydrodynamic diameter of the particles changed with pH due to the latex-to-microgel transition. This is shown in Figure 2 for PDEA-1, 2, 4, 9, 10, and 11. Most microgels showed features consistent with three specific pH regions. Particle size initially stayed constant within a pH range of 2.0 and 4.0, as expected. Particle size then

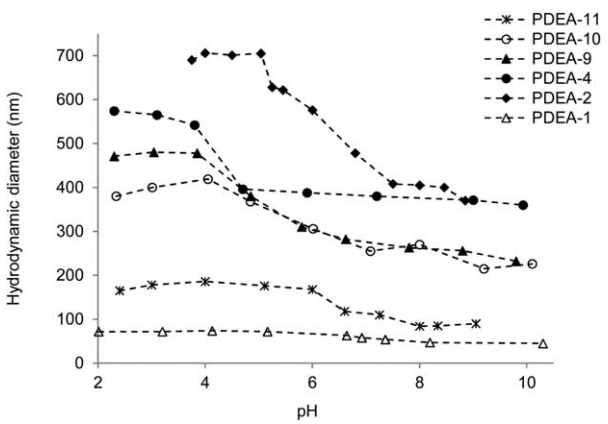

Figure 2. Hydrodynamic diameter with respect to pH for some of the microgels.

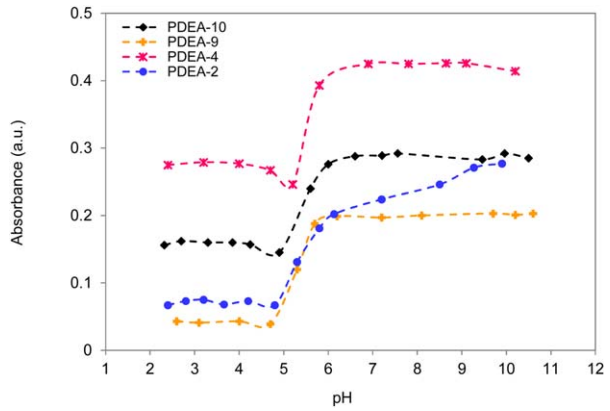

Figure 3. The variation of visible region absorbance with pH for some PDEA microgel dispersions. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

proceeded to decrease slowly between pH values of 4.5 and 7.5, consistent with the range reported in the literature in which the PDEA homopolymer begins to lose protons.[1] In addition, it suggests that the stable cationic charge of the QDMA moiety may have led to soft reduction in size even PDEA moiety shrinks by losing protons. Particle size remained roughly constant in the last region. However, the PDEA-4 microgel particles decreased sharply in size, which was unsurprising given that they were prepared without QDMA monomers. The hydrodynamic diameter distribution curves of the microgel dispersions at pH 8.0 recorded by zetasizer are given in Supporting Information Figure S3. SEM images of the microgels in dehydrated form (Supporting Information Figure S4) indicates the particles have a spherical morphology. However, the surfaces of some particles that become soft due to cationic comonomer deformed and stuck to each other during drying.

The pH-responsive behavior of the microgels was also investigated by using UV–vis spectrophotometer. Figure 3 gives the variation of visible region absorbance with pH for some microgels. A mild increase was observed in the absorbance with increasing pH between 4.5 and 7.5 for PDEA-2, 9 and 10

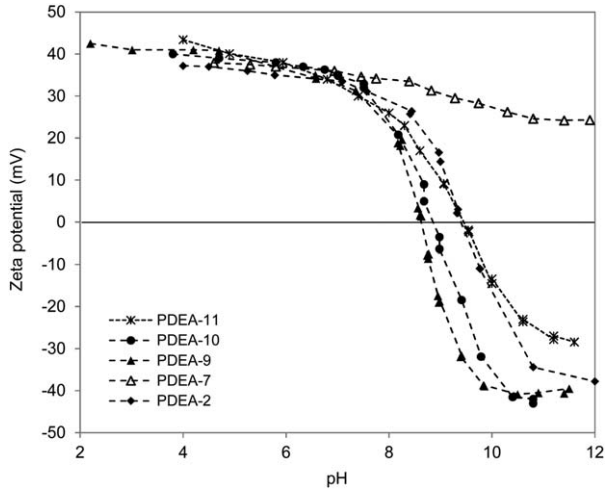

Figure 4. Zeta potentials with respect to pH curves for some of the PDEA microgels synthesized with QDMA monomers.

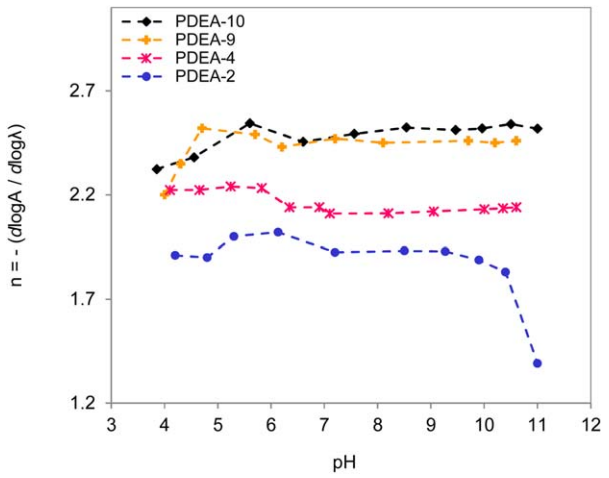

Figure 5. Variation of the *n*-value of some PDEA microgels with pH. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

microgels while PDEA-4 had relatively sharp increase (Figure 3). This is consistent with the hydrodynamic diameter change in the same pH range (Figure 2).

The IEPs obtained from zeta potential measurements are summarized in Table I, while some of the zeta potentials are plotted against the obtained pH curves in Figure 4. All those containing QDMA monomers had IEPs higher than 8.50. In fact, by modifying reaction parameters, this value could be increased further, all the way up to 12.0. Again, PDEA-4 has a lower IEP value.

As we know from the literature, the IEP of a polymer particle is largely related by the nature of the stabilizer chosen for the polymerization medium.[1] This is consistent with the previously observed behavior of the copolymers, wherein the QDMA moieties of most of the microgels were protonated even above a pH of 9.0, lending high colloidal stability.

Colloidal stability was investigated by determining the stability parameter, n from turbidity–wavelength measurements which is an effective method for microgel dispersions.[44,45] For some microgels, typical plots of $\log(A)$ versus $\log(\lambda)$ data is given in Supporting Information Figure S5. The plots of the variation of stability parameter, n with pH is shown in Figure 5. It is well known that the magnitude of n is very sensitive to changes in particle size.[44,49] As seen in Figure 5, constant n value indicated the PDEA-4, 9 and 10 microgel dispersions remain stable at all pH values studied. However, the presence of an abrupt decrease observed for PDEA-2 indicated the microgel dispersion was aggregated above pH 10.4. The colloidal stability of microgel particles depends on the balance of van der Waals attraction and electrostatic or steric repulsion.[49] In addition, without stabilization, colloidal particles usually tend to aggregate due to van der Waals attractive force. It seems that this force probably become dominant between the long carbon chains in the PDEA-2 microgel with increasing the pH of the medium.

Effects of the Amount of DEA on Polymer Characteristics

The effects of the amount of DEA on particle size, zeta potential, and IEP were investigated by varying the amount of DEA

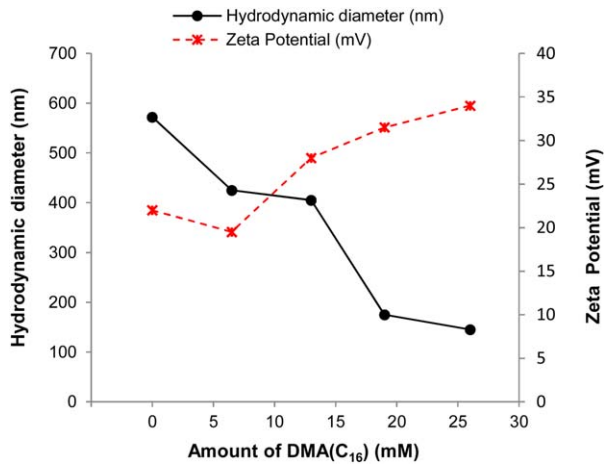

Figure 6. Effects of the amount of DMA(C_{16}) on the particle size and zeta potentials of the microgel particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

used between 1.2 and 4.8 mL. Particle size increased with the amount of DEA, as expected.[50] As known from the literature,[51,52] the amount of the main monomer is only important in the final stage in emulsifier-free emulsion polymerization because the actual concentration remains constant during nucleation and flocculation, during which new particles are generated. However, in the final stage, the number of primary particles remains constant while the particles themselves continue to grow by absorbing monomer droplets from the polymerization mixture. This means that greater amounts of monomer actually lead to larger particles. However, as the amount of DEA continued to increase, stabilization of the increasingly hydrophobic particles decreased and the particles began to aggregate. Similarly, the IEP values decreased from 10.8 to 9.41 (Table I).

Effects of the Amount of Cationic Comonomer on Polymer Characteristics

The effects of the amount of cationic monomer on particle size were investigated by varying the amount of DMA(C_{16}) between 0.0 and 26 mM, as shown in the size and zeta potential trends presented in Figure 6. Particle size considerably decreased as the amount of cationic comonomer increased, a typical response for emulsifier-free emulsion polymerization utilizing ionic comonomers.[53]

Particle size is known to be affected by the nucleation process in this kind of polymerization. However, no matter whether the nucleation mechanism is homogenous,[54] oligomer micellization,[54,55] or precipitation,[56,57] the most important step is the very first one. An increase in the amount of cationic monomer leads to an increase in the nucleation rate in this stage, so long as the amount of other reactants is held constant. Because of this, a higher number of stabilized particles form and the produced particles are smaller.

Conversely, the zeta potentials significantly increased with the amount of cationic monomer (Figure 6), contributing to colloidal stability. For example, an increase in DMA(C_{16}) concentration from 6.5 to 26.0 mM lead to an increase in zeta potential of 14.7 mV. IEP values also increased with cationic monomer amount, as expected. For example, an increase in DMA(C_{16}) concentration to 26.0 mM gave IEP values higher than 12.0.

Effects of the Type and Chain Length of the QDMA Monomer on Polymer Characteristics

PDEA particle size decreased with QDMA alkyl group chain length from 405 to 275 nm (Table I). A similar decrease was observed when the benzyl group was used instead (Figure 7). This may be due to the corresponding decrease in hydrophobic character for shorter chains. In addition, given the formation mechanism, the hydrophobic segments typically form the core of the particles while the ionic groups in the hydrophilic segments tend to be found on the shell surface.[58,59] Therefore, a reduction in hydrophobicity of the comonomer decreases the volume of the particle core, and, consequently, particle diameter.

The structure of QDMA monomer has also a significant effect on colloidal stability of the microgel dispersion. As shown in Table I and Figure 7, the microgel prepared with DMA(Bz) has the zeta potential comparable to DMA(C_{16}) microgel and the particle size significantly smaller than DMA(C_{16}). So, this indicates that DMA(Bz) comonomer produced the most stable microgel dispersion. This result is also supported by stability parameter measurements given in Figure 5.

Effects of the Water/Monomer Ratio on Polymer Characteristics

The effect of the water to monomer ratio was analyzed by varying the amount of water used over a range of 50–150 mL, giving a ratio of 20.81–62.44, respectively. DMA(C_{16}) was used as the quaternary ammonium monomer in these experiments.

The obtained Zetasizer data is given in Figure 8, and shows a significant initial decrease in particle size as the water/monomer ratio was increased from 20.81 to 31.22. Further decrease was observed between the ratio of 31.22 and 41.63. The smallest particles, about 46 nm in diameter, were obtained with a ratio of 41.63, above which point particle size remained constant.

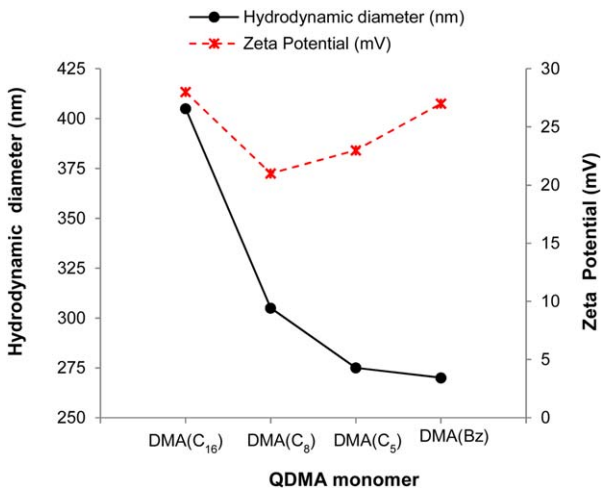

Figure 7. Effects of type and chain length of the QDMA monomer on particle size and zeta potentials of the microgel particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

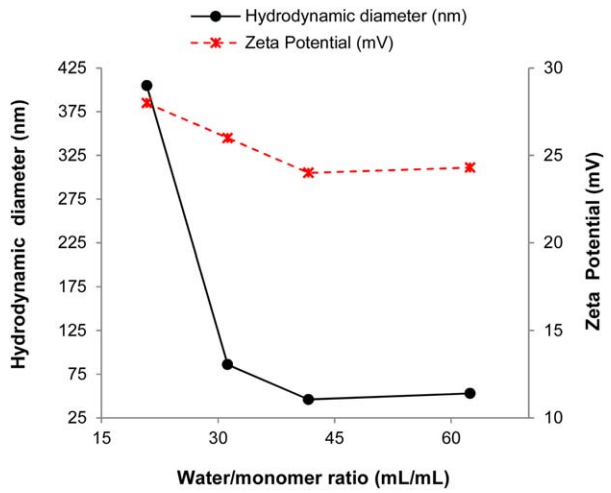

Figure 8. Effects of the water/monomer ratio on particle size and zeta potentials of the microgel particles. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

This is actually consistent with previous observations relating to emulsifier-free emulsion polymerization, given that this change reflects a decrease in the monomer to polymerization medium ratio. Additionally, the specific surface area of the particles increased with decreasing particle size, which, as suggested by the literature, probably leads to the observed decrease in zeta potential.[50]

CONCLUSION

This study reported the preparation of emulsifier-free PDEA microgels with clean and usable surfaces, synthesized by using cationic monomers with *n*-hexadecyl, *n*-octyl, *n*-pentyl, or benzyl groups attached to their quaternary ammonium moieties. The QDMAs utilized not only acted as monomers, but also as polymerizable surfactants, providing high colloidal stability even at high pH values. Among these comonomers, DMA(Bz), provided the best stabilization. The hydrodynamic diameters of the particles ranged from 46 to 425 nm at pH 8.0, depending on the synthetic conditions. Meanwhile, aqueous electrophoresis studies indicated that most of the microgels had cationic surface charges up to a pH of 9.0. Overall, the stable cationic charge of the quaternary ammonium monomers increased the latex-to-microgel swelling transition to a pH higher than that dictated by the known pK_a of 7.3 of linear PDEA homopolymer. In addition to biocompatibility, this type of microgels has the potential to be used for antimicrobial purposes due to have tertiary amine groups.

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