

## Multi-responsive microgel of a water-soluble monomer via emulsion polymerization

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**ABSTRACT:** Microgel of a water-soluble monomer [2-(*N*-morpholino)ethyl methacrylate (MEMA)] was successfully prepared in aqueous media via emulsion polymerization by using a novel water-soluble block copolymer as stabilizer. Characterization studies confirmed monodisperse spherical morphologies of microgels with a diameter of 280 nm at neutral pH. These microgels exhibited multi-responsive behavior by responding solution pH, temperature, ionic strength, type of dispersing media, and magnetic particles. It swells well at low pH (<6.0) and at low temperature, but shrinks above pH 6.0, or even more shrinks with salt addition at neutral and basic conditions. In addition, the hydrodynamic diameter of PMEMA microgel was decreased gradually at basic and neutral pH when solution temperature was increased up to the lower critical solution temperature of PMEMA (LCST, 35°C), but microgel diameter did not change much above LCST. Multi-responsive behavior of PMEMA microgel was investigated by using dynamic light scattering, UV-Vis spectrophotometer and zeta potentiometer. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 42072.

**KEYWORDS:** cross-linking; emulsion polymerization; microgels; stimuli-sensitive polymers

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### INTRODUCTION

Microgels are a class of soft colloidal particles consisting of cross-linked polymer chains. They can be fully swollen or collapsed in good and poor solvent, respectively. Their swelling-shrinking degrees and morphologies depend on their ionic/nonionic or hydrophilic/hydrophobic natures, degree of cross-linking, and external conditions. They can be readily prepared to give responsive behavior to solution pH, temperature, ionic strength, solvent quality, light, etc.<sup>1–7</sup> Microgels are usually prepared by precipitation polymerization,<sup>1,8</sup> anionic copolymerization,<sup>9</sup> emulsion polymerization,<sup>1,10,11</sup> inverse emulsion polymerization,<sup>12</sup> cross-linking neighboring polymer chains.<sup>13</sup> Due to their impressive features, these materials have great application potentials such as in the surface coating industry, pollution control, drug and gene delivery,<sup>14–19</sup> biotechnology,<sup>19–24</sup> magnetic studies,<sup>25</sup> membrane technology,<sup>26</sup> sensor technology,<sup>27</sup> catalysis,<sup>28,29</sup> microreactor, and hybrid material systems.<sup>30</sup>

A number of examples of both thermo-responsive and pH-responsive aqueous microgels have been reported over the past decade or so. The former are usually based on poly(*N*-isopropylacrylamide) (PNIPAM) which exhibits a lower critical solution temperature (LCST) of around 32–33°C.<sup>10,31–34</sup> This LCST is responsible for the thermo-responsive character of PNIPAM particles which are particularly attractive for use in the context

of drug delivery. Many other related comonomers were also copolymerized with NIPAM to influence the swelling behavior of thermo-responsive microgels. These include *N*-acryloyl glycine, acrylic acid, 2-aminoethyl methacrylate, etc.

pH-responsive microgels usually comprise weak acidic and/or weak basic monomers, with hydrophobic monomer incorporated in some cases.<sup>35–37</sup> These include (meth)acrylic acid-based alkali-swelling microgels, NIPAM-based copolymer microgels containing either acidic or basic comonomers, and both tertiary amine methacrylate- and vinylpyridine-based acid-responsive microgels. Polyampholytic microgels have also been reported by copolymerization of methacrylic acid and amine-based methacrylates as anionic and cationic monomers, respectively.<sup>37</sup> The pH-induced volume phase transitions of these microgels occur at their isoelectronic point, while the particles were in swollen state in both low and high solution pH. For example, pH-responsive polyampholyte microgel (PMAA/PDEA) having diameter of 200–300 nm was synthesized via emulsion polymerization. These microgels collapsed at intermediate pH but exhibit hydrophilic character at acidic and basic pH in aqueous medium. Hydrodynamic radius of sterically stabilized microgels was 120 and 200 nm at pH 2.0 and 10.0, respectively.

Another type of microgel is salt-responsive microgel which is produced from a neutral water-soluble polymer having response

to ionic strength. PNIPAM microgels<sup>32</sup> and poly[NIPAM-*co*-2-(*N*-dimethylamino)ethyl methacrylate], P(NIPAM-*co*-DMA), microgels were in this class.<sup>33</sup> Such microgels showed (de)swelling behavior at different temperature by addition of salt in their aqueous dispersion.

Microgels can also be coated with magnetic nanoparticles. These magnetic nanoparticle coated-microgel hybrid systems are of great interest for researchers from a wide range of disciplines such as in catalysis resonance imaging, biotechnology/biomedicine and magnetic fluids. These observation indicates that such microgels might have a potential in waste-water treatment as novel picker for magnetic nanoparticle contaminants.<sup>38,39</sup>

In addition to these studies, dual-responsive microgels are also reported in the literature.<sup>40,41</sup> For example, Liu *et al.* were prepared a microgel having temperature-sensitive cores and pH sensitive shell by copolymerizing *N,N*-diethylacrylamide and methacrylic acid microgels [P(DEAAm-*co*-MAA)] in water. In this study, thermo-responsive part is DEAAm and pH-responsive part is MAA.<sup>40</sup> PNIPAM based dual responsive microgels were also reported by using either acrylic acid or vinylacetic acid as comonomers. In these systems, the PNIPAM segments of the microgel are the thermo-responsive parts and AA or VAAc residues of the microgels enable the systems to be responsive to solution pH.<sup>41</sup>

There is only one example in the literature on multi-responsive microgel which consists of only one monomer and responds more than three external stimuli as reported by us.<sup>42</sup> In that study, a series of novel poly[2-(*N*-morpholino)ethyl methacrylate] microgels with the size between 60 and 360 nm were synthesized via dispersion polymerization in hexane. After purification, the freeze-dried microgels were redispersed in water and their multi-responsive behaviors to external stimuli were investigated in detail.

Beside the great multi-responsive nature of these microgels, there is an important disadvantage of the method used in the synthesis of PMEMA microgels. It is the use of an organic solvent (hexane) as dispersing media. Hexane is not a biocompatible liquid. That requires additional purification process and special stabilizer for the related microgel. These microparticles are good candidate for different applications such as in the area of biotechnology, pharmacy, chemistry. They can be used as drug carrier or drug releasing system, micro-host or nanocage for nanometal production, picker for inorganic nanoparticles, etc. Therefore, it must be avoided the use of hexane. In order to enhance the impact of the biotechnological applications of PMEMA microgels, it is necessary to carry out their synthesis in aqueous media.

Here in, we report successful synthesis of poly[2-(*N*-morpholino)ethyl methacrylate] microgel (PMEMA) in aqueous media by using a novel ABC type triblock copolymer as stabilizer. These microgel particles were made of a water-soluble monomer which has a weak basic character, and stimuli responsive and low toxic nature. Thus, PMEMA microgel has a response to external stimuli including pH, temperature, ionic strength, and magnetic particle. Steric stabilization of PMEMA microgels was provided by using a

poly(ethylene oxide)-*block*-poly[2-(*N*-diethylamino)ethyl methacrylate]-*block*-poly(2-methacryloyloxyethyl phosphorylcholine) (PEO-*b*-PDEA-*b*-PMPC) triblock copolymers.

## EXPERIMENTAL

### Materials

2-(*N*-morpholino)ethyl methacrylate (MEMA, Polysciences), 2-(*N*-diethylamino)ethyl methacrylate (DEA, Aldrich) and ethylene glycol dimethacrylate (EGDMA, Aldrich) monomers were purged through an basic alumina column to remove the inhibitor. Ammonium persulphate (APS, Fluka) as an initiator and poly(ethylene glycol)methyl ether methacrylate (PEGMA, Aldrich) as costabilizer were used without further purification. Double-distilled water was used as dispersing media for the emulsion polymerization. Poly(ethylene oxide)-*block*-poly[2-(*N*-diethylamino)ethylmethacrylate]-*block*-poly(2-methacryloyloxyethyl phosphorylcholine) (PEO<sub>44</sub>-*b*-PDEA<sub>46</sub>-*b*-PMPC<sub>50</sub>,  $M_n = 25,500$  g/mol,  $M_w/M_n = 1.27$ ) triblock copolymer was used as novel steric stabilizer. It was synthesized via atom transfer polymerization (ATRP) by using the recipe and the pathway reported by Armes and co-workers by reversing the comonomer sequence.<sup>43</sup> For the synthesis of ATRP macroinitiator, methoxy-capped poly(ethylene glycol) (PEG<sub>2000</sub>), 2-bromoisobutyryl bromide, triethyl amine and anhydrous toluene were purchased from Aldrich and used without further purification. 2-Methacryloyloxyethyl phosphorylcholine (MPC), Cu(I)Br, 2,2'-bipyridyl (bpy) and methanol were also purchased from Aldrich and used without further purification. FeCl<sub>4</sub>·4H<sub>2</sub>O and FeCl<sub>3</sub>·6H<sub>2</sub>O (Merck), NH<sub>4</sub>OH (Aldrich) was used in the synthesis of magnetic nanoparticles.

### Synthesis of PMEMA Microgels via Emulsion Polymerization

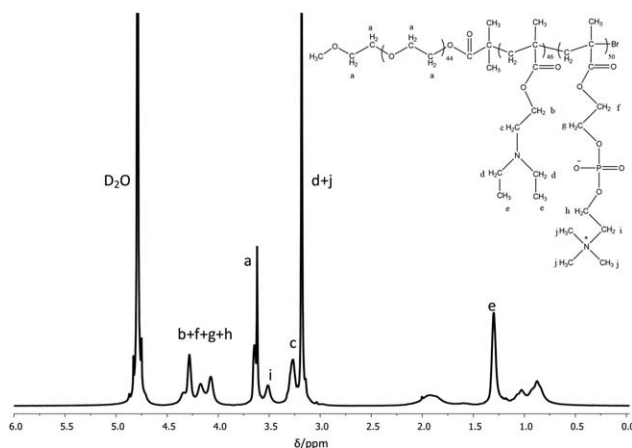
Polymerization was carried out in a 100 mL two-necked round-bottomed flask equipped with a reflux condenser and sealed with rubber septum. PEO-*b*-PDEA-*b*-PMPC triblock copolymer stabilizer (0.5 g) and water (22 mL) were first transferred to the reaction flask. The solution was purged with nitrogen for 15 min to remove any oxygen. Previously degassed MEMA monomer (3.0 mL) and EGDMA cross-linker (0.5 mol % based on MEMA) were added into the flask under a nitrogen purge. The system temperature was fixed at 70°C in an oil bath just before addition of the degassed solution of the APS initiator (50 mg in 3 mL deionized water).

### Purification of Microgels

Dialysis method was used to remove unreacted monomers and excess stabilizer or surfactants. In dialysis process, the microgel dispersion was filled in a cellulose dialyzing tubing (MWCO, 12–14000 Da) and kept in a water bath for 5 days by replacing water in the bath with freshly distilled water in every 24 h.

### Characterization

Comonomer composition of triblock copolymer was determined by using a Bruker 500 MHz Avance II NMR instrument. The proton NMR spectrum was recorded in D<sub>2</sub>O solvent by adjusting the solution pH 2.5 with concentrated DCl/D<sub>2</sub>O solution. The actual DP's of each block were also calculated from NMR spectra by using PEO block as end group.

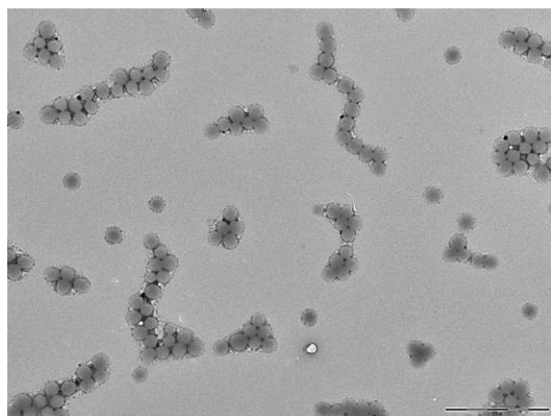


**Figure 1.**  $^1\text{H}$  NMR spectrum of  $\text{PEO}_{44}\text{-}b\text{-PDEA}_{46}\text{-}b\text{-PMPC}_{50}$  triblock copolymer in  $\text{D}_2\text{O}$ .

Dynamic light scattering (DLS) was used to determine the hydrodynamic diameters and the polydispersity indexes ( $\text{PDI} = \mu_2/\Gamma^2$ ) of all PMEMA microgel dispersions. DLS was conducted on an ALV/CGS-3 compact goniometer system (Malvern, U.K.) equipped with a 22 mW He-Ne laser operating at  $\lambda_0$  632.8 nm, an avalanche photodiode detector with a high quantum efficiency, and an ALV/LSE-5003 multiple  $\tau$  digital correlator electronic system. The temperature was controlled using both a cell and external bath acting through the sample cell.

The morphologies of the microgel particles were also investigated by using transmission electron microscopy (TEM). A single drop of dilute solution of microgel (<0.001 wt %) was dropped on a Formvar-coated copper TEM grid and dried overnight at room temperature. TEM micrographs were acquired at 80 kV (Jeol, JEM-1220 Electron Microscopy).

Turbidimetric studies of PMEMA microgels were carried out by using UV-Vis spectrophotometer (Perkin Elmer Lambda-35) at 500 nm as a function of solution pH. A small temperature probe was immersed in the upper part of the stirred copolymer solution, and the solution temperature was increased slowly from 15 to 45°C. The temperature was kept at a designed temperature for 2 min before each measurement. According to both



**Figure 2.** TEM micrograph of PMEMA microgel (scale bar: 2  $\mu\text{m}$ ).

DLS and UV-Vis measurements, 2 min is enough to reach the (de)swelling equilibrium for PMEMA microgels.

A Zetasizer Nano ZS (Malvern Instrument, U.K.) was used to measure the zeta potential of microgels as a function of pH. The solution pH of PMEMA microgel samples was adjusted with HCl and KOH, and measurements were repeated at least three times.

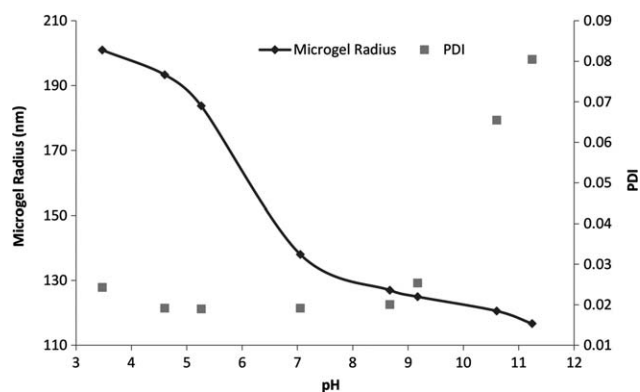
The titration of a 0.2% microgel solution was carried out using 0.5–1.0 M NaOH solution. pH was measured by using Inolab WTW series pH 720 model pH meter. The calibration was carried out using pH 4.0, 7.0, and 10.0 buffer solutions (Aldrich).

## RESULTS AND DISCUSSION

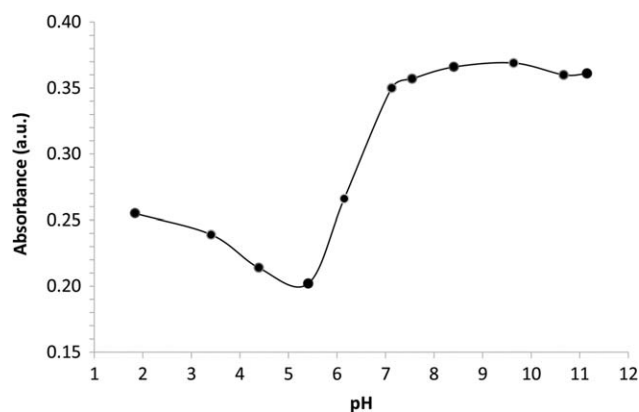
### Synthesis of PMEMA Microgels

Poly(ethylene oxide)-*block*-poly[2-(*N*-diethylamino)ethyl methacrylate]-*block*-poly(2-methacryloyloxyethyl ethyl phosphorylcholine) block copolymer stabilizer was synthesized via atom transfer polymerization (ATRP) by using the recipe and the pathway reported by Armes and co-workers by reversing the comonomer sequence.<sup>43</sup> The structure of the stabilizer was characterized with  $^1\text{H}$  NMR spectroscopy.  $^1\text{H}$  NMR spectrum of the triblock copolymer indicated full conversion of the monomers due to observation of no residual of monomer methylene protons at  $\delta$  5.5–6.0 ppm. The comonomer composition of the triblock copolymer (Figure 1) was determined by comparing the "peak a" integral of the  $-\text{O}-\text{CH}_2-\text{CH}_2-$  protons of PEO block at  $\delta$  3.6 ppm with both peak integrals of the six protons (peak e) in the DEA residues at  $\delta$  1.3 ppm and peak integrals of nine protons (labelled j) of the MPC residues at  $\delta$  3.2 ppm. As calculated from molecular weight, the PEO has an actual degree of polymerization (DP) of 44. This DP value of PEO block (repeating ethylene oxide units) was used as end group to determine the actual degree of polymerization for second and third blocks in the PEO-*b*-PDEA-*b*-PMPC triblock copolymer. The DP values were determined to be 44, 46, and 50 in the triblock copolymer, respectively, by using the protons of PEO block at  $\delta$  3.6 ppm as end group.

PEO-*b*-PDEA-*b*-PMPC triblock copolymer can form micelle at  $\text{pH} > 7.5$  by the middle block forming micelle core and the outer blocks forming hydrated coronas. Nitrogen atoms of



**Figure 3.** Variation of hydrodynamic radius and PDI values of PMEMA microgel depending on pH.



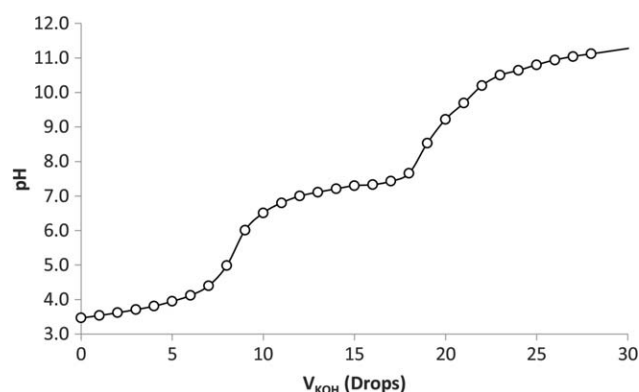
**Figure 4.** Change of absorption of PMEMA microgel dispersion as a function of pH.

PDEA blocks are in deprotonated form at  $\text{pH} > 7.5$  and PDEA blocks become insoluble due to dehydration. But both outer blocks show hydrophilic characters at all pH range. Thus, this block copolymer was successfully used in the stabilization of PMEMA microgels in aqueous media.

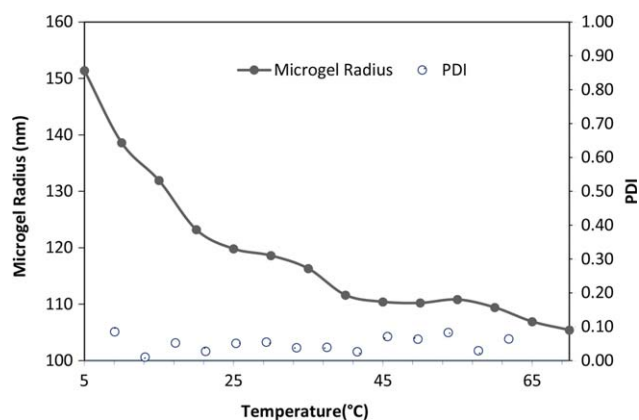
PMEMA homopolymers are soluble at room temperature but have cloud points between 34 and 53°C depending on their  $M_n$  values as reported before.<sup>44</sup> Thus, its polymer is not soluble at 60°C. We have taken this phase separation as an advantage to prepare PMEMA microgels in aqueous media via emulsion polymerization. Successful stabilization of microgel was provided by using PEO-*b*-PDEA-*b*-PMPC triblock copolymer as a novel stabilizer. Cross-linking degree was chosen to be 0.5 mol % based on MEMA monomer. The diameter of hydrated microgel was  $\sim 280$  nm and the PDI value was 0.01 at neutral pH. Figure 2 shows TEM image of the PMEMA microgel in dehydrated form and indicates monodisperse particle size distributions with a diameter of around 200 nm. The stabilization of cross-linked MEMA homopolymer chains was successfully provided by the physical adsorption of triblock copolymer onto spherical crosslinked PMEMA.

#### pH-Induced Swelling Behavior

The effect of pH on the hydrodynamic radius of PMEMA microgel was investigated by DLS studies. The hydrodynamic



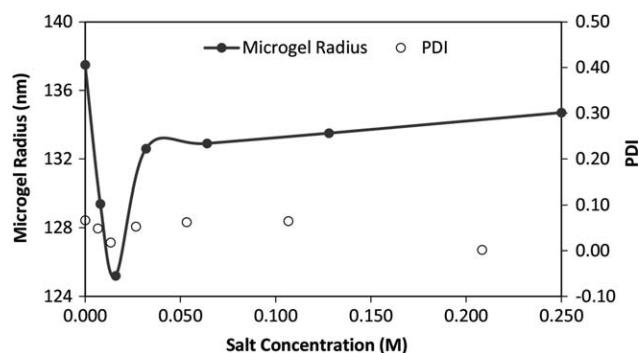
**Figure 5.** Titration curves of PMEMA microgel at 25°C (apparent  $\text{p}K_a = 7.2$ ).



**Figure 6.** Variation of hydrodynamic radius and PDI values of PMEMA microgel with temperature. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

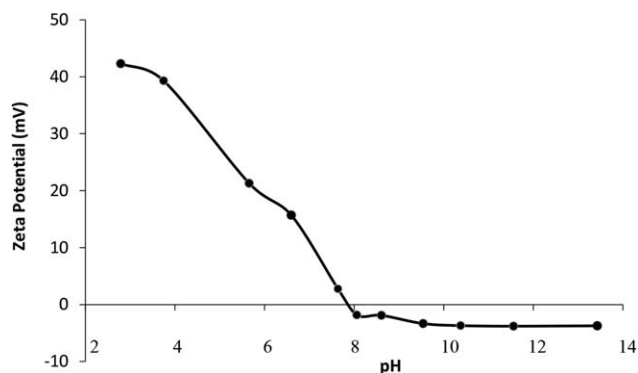
radius of PMEMA microgel in aqueous media at pH 3.5, 7.1, and 11.2 were determined to be 201, 140, and 117 nm, respectively (Figure 3). The shrinking ratio of PMEMA microgel was calculated to be 41.8% when pH was increased from pH 3.5 to 11.2. The largest sizes of microgels at low pH should be due to ion-dipole interaction between cationic microgels and water. At this pH, morpholino groups of PMEMA microgel (linear PMEMA having a  $\text{p}K_a$  around 4.9) are in protonated form which causes more hydration. DLS studies indicated that PMEMA microgel had a monodisperse size distributions in the both acidic and basic aqueous medium. When the pH of medium was adjusted to neutral or basic pH, microgel was in shrunk state due to deprotonation and dehydration of PMEMA. Critical swelling-deswelling pH of the microgel particles was also determined to be around pH 7.5 by using UV-Vis spectrophotometer (Figure 4). This pH is higher than the  $\text{p}K_a$  of linear PMEMA homopolymer conjugate. This difference may come from stabilizer which has PDEA residues with a  $\text{p}K_a$  around 7.4.

In order to understand its high critical swelling-deswelling pH, microgel dispersion was also titrated by using KOH solution to determine its  $\text{p}K_a$ . Figure 5 shows titration curve for PMEMA microgel at 25°C. The related apparent  $\text{p}K_a$  value was determined to be 7.2 at 25°C. This value is well agree with the critical swelling-deswelling pH of the microgel particles determined



**Figure 7.** Dependence of hydrodynamic radius of PMEMA microgel on NaCl concentration at pH 7 and 20°C.





**Figure 8.** Zeta potentials of PMEMA microgel with variation of pH at room temperature.

by UV-Vis study. The  $pK_a$  value for a linear PMEMA homopolymer was 4.9 as reported by us before.<sup>44</sup> The  $pK_a$  of PMEMA microgel was higher than that of the linear PMEMA homopolymer. This difference might be due to the ABC type triblock copolymer stabilizer having PDEA residues with a  $pK_a$  around 7.4,<sup>44</sup> and cross-linked and spherical-morphology of the microgel.

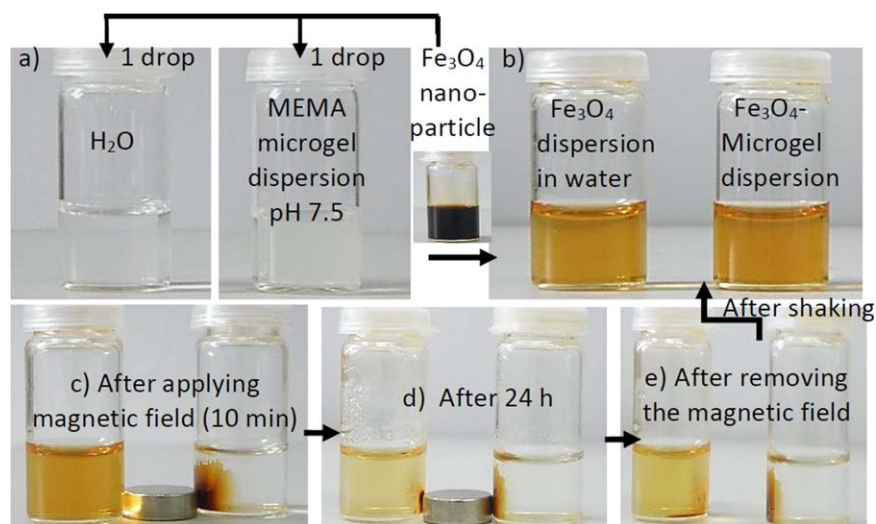
#### Temperature-Induced Size Change

PMEMA homopolymer is weak polybase. It is soluble at acidic and neutral pH at room temperature but less soluble at neutral and basic pH values.<sup>44,45</sup> As PMEMA has a response to solution temperature and thus has a volume phase transition temperature (VPTT), PMEMA microgel has thermo-responsive character as well. Because of predominated hydrophobic forces, it shrinks above the volume phase transition temperature (VPTT or LCST for linear PMEMA homopolymer) at aqueous media. On the contrary, hydrophilic forces are effective below the VPTT and microgel is in a swollen state. Dynamic light scattering (DLS) was used to determine the phase transition tempera-

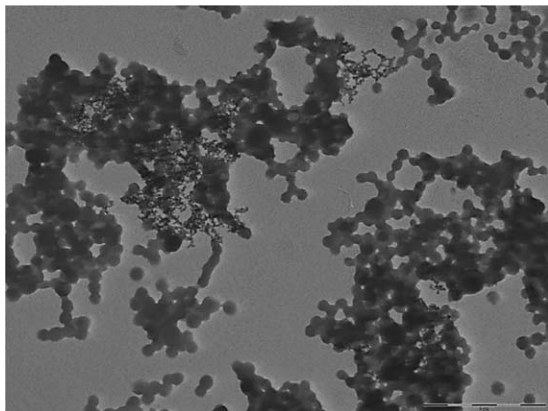
ture of temperature-sensitive particles. The DLS results based on hydrodynamic radius of PMEMA microgel were given in Figure 6. Until the temperature reached to the LCST (about 35°C), the size of the microgel gradually decreases at basic and/or neutral dispersions. Microgel size does not change too much above the LCST. In acidic solution, all the nitrogen atoms of PMEMA are in protonated form, thus, the hydrodynamic diameter of PMEMA microgel does not change. Hydrodynamic radius of PMEMA microgel at pH 9.3 was determined to be 140 (PDI: 0.01), 116 (PDI: 0.04), 110 nm (PDI: 0.02) at 10, 35 and 45°C, respectively. Radius of PMEMA microgels properly decreased with the increase in temperature. These results indicated the thermo-sensitive nature of PMEMA microgels. Microgel exhibited an additional interesting behavior at around 55°C. This should be related to glass transition temperature ( $T_g$ ) of PMEMA chains which were softened at this temperature.

#### Salt-Induced Swelling/Shrinking Behavior

As reported in our previous studies, PMEMA homopolymer can also be precipitated over pH 6 by adding salt such as  $\text{Na}_2\text{SO}_4$ ,  $\text{K}_2\text{CO}_3$ .<sup>44</sup> Thus, the addition of electrolytes in PMEMA microgel dispersion should cause a shrinking of microgel due to its dehydration. To examine this (de)swelling behavior, the size of microgel was measured in the presence of NaCl at different concentrations at 20°C by using DLS (Figure 7). The size of microgel was decreased via an increase in salt concentration, but not as much as we expected. There is an unusual change on the diameter of microgel in aqueous media with salt addition. First, the diameter decreases sharply at the beginning with a little salt addition (16 mM  $\text{Na}_2\text{SO}_4$ ) but it starts to increase with further salt addition (32 mM  $\text{Na}_2\text{SO}_4$ ). When salt concentration was more than 32 mM, the diameter of microgel did not change so much. We assume that the unusual increase on diameter with salt addition (between 16 and 32 mM) might be due to PMPC-chain of the stabilizer on the microgel surface. As reported in the literature, in contrast to polyelectrolytes, the



**Figure 9.** Interaction of PMEMA microgel with magnetic particles: (a) before transferring the  $\text{Fe}_3\text{O}_4$  magnetic nanoparticle dispersion into both water and aqueous PMEMA microgel dispersion (pH >7.5), (b) after transferring the magnetic nanoparticle dispersion, (c) after applying the magnetic field for 10 min, (d) after applying of the magnetic field for 24 h, and (e) after removing the magnetic field (redispersibility). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 10.** TEM image of interaction of PMEMA microgel with  $\text{Fe}_3\text{O}_4$  magnetic particles (scale bar: 1  $\mu\text{m}$ ).

polybetaines chain-expand with increasing salt concentration.<sup>46</sup> PMPC is a betaine-chain and it has an inverse response to ionic strength.

#### Interaction with Magnetic Nanoparticle

$\text{Fe}_3\text{O}_4$  magnetic nanoparticles being used in the interaction with PMEMA microgel was prepared via sedimentation process as reported in the literature.<sup>38</sup> The resulting  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles had an average hydrodynamic radius of 27.5 nm with a broad polydispersity index value (PDI: 0.21). The  $\text{Fe}_3\text{O}_4$  magnetic particle dispersion exhibited a positive zeta potential at around pH 7.5 while microgel dispersion exhibited a little negative zeta potential (Figure 8) under similar conditions. Thus, we expected a good electrostatic interaction of  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles with PMEMA microgel particles due to having opposite surface charges at pH 7.5. It was also expected that the nanoparticle could gather around the microgel particle due to ion-dipole interactions between positively charged  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles and polar morpholino residues of PMEMA microgel.

To test these hypotheses, first, microgel dispersion was prepared at pH >7.5 [Figure 9(a)] and little amount of concentrated  $\text{Fe}_3\text{O}_4$  magnetic particles dispersion (1 drop, 10 wt %) was added [Figure 9(b)]. At the same time, as the control sample, the same procedure was performed with the same amount of water in the absence of microgel. After applying magnetic field on both dispersions at the same time, magnetic nanoparticle coated microgel gathered near by magnet in 10 min [Figure 9(c)]. The color of the solution became transparently like water. During the same period, the same result was not observed for water- $\text{Fe}_3\text{O}_4$  dispersion. After 24 h, very little substance was gathered around a magnet in the absence of microgels [Figure 9(d)]. When the magnetic field was removed, the gathered magnetic particles were quickly redispersed in the absence of microgel, but the microgel-magnetic particle system did not dispersed without shaking [Figure 9(e)]. The TEM image did not support first assumption. As seen in TEM image (Figure 10), the magnetic nanoparticles were located among microgel particles (not on the surface). Thus, such aggregate-type dispersion indicates electrostatic interaction between positively charged  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles and slightly negatively charged microgel par-

ticles. This interaction caused dispersed-aggregation and clustering of magnetic particles among microgel particles. Such clustering increased response to magnetic field and allowed us to separate these aggregates from aqueous phase very easily via applying magnetic field.

#### CONCLUSION

Monodisperse microgel of a water-soluble monomer, namely 2-(*N*-morpholino)ethyl methacrylate, was successfully prepared via emulsion polymerization by using a novel ABC type water soluble triblock copolymer as novel emulsifier. This microgel had multi-responsive nature in aqueous media. It had response to solution pH, temperature, ionic strength, and magnetic particles in the medium. It swelled very well both in acidic conditions and at low temperatures, but shranked at neutral and basic conditions, or even more shranked with the addition of tiny amount of salt at pH >7.

Additionally, this microgel swelled more and more at basic and neutral pH conditions by decreasing temperature from room temperature to 5°C but shranked when solution temperature was increased up to the lower critical solution temperature of poly[2-(*N*-morpholino)ethyl methacrylate] (LCST, 35°C). Further increase on temperature above LCST did not change the diameter too much. These microgels deswelled by the addition of tiny amount of salt but surprisingly it started to swell by further salt addition and the size did not change any more by increasing salt concentration over 32 mM. This is the first observation with a microgel having both swelling and deswelling behavior with just increasing ionic strength of the medium. It indicated that it showed dehydration and followed by hydration by just increasing ionic strength of the medium. They also interacted with  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles very well and behave as novel picker and allowed faster removal.

This novel poly[2-(*N*-morpholino)ethyl methacrylate] microgel can be considered to be promising materials in various applications such as in biomedical applications, in waste water treatment, and in water purification. They can also be used as a host in the synthesis of nanometal particles. Our results on the preparation and model application studies based on this microgel-nanometal hybrid system are in the preparation for further publications.

#### ACKNOWLEDGMENTS

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