Polymer 72 (2015) 361-367

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer

Developing recyclable pH-responsive magnetic nanoparticles for oil—water separation



polyme

Xiaofeng Wang, Yi Shi, Robert W. Graff, Doyun Lee, Haifeng Gao^{*}

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame, IN, USA

ARTICLE INFO

Article history: Received 13 November 2014 Received in revised form 9 December 2014 Accepted 23 December 2014 Available online 3 January 2015

Keywords: Hybrid magnetic nanoparticle pH-responsiveness Oil-water separation

ABSTRACT

Hybrid magnetic nanoparticles (MNPs) with well-defined core-shell structure, pH-tunable interfacial activity and strong magnetic responsiveness were developed as recyclable stabilizers for oil–water separation. The Fe₃O₄ magnetic core was synthesized using a solvothermal method involving hydrolysis of Fe(II) and Fe(III) salts in basic condition, followed by surface-initiated atom transfer radical polymerization (SI-ATRP) of dimethylaminoethyl methacrylate to grow the PDMAEMA shell. The magnetic core allowed rapid separation of the oil droplets from emulsions under external magnetic field, while the pH-responsive polymer shell offered the hybrid MNPs tunable interfacial activity to form and break Pickering emulsion reversibly for recyclable use of the hybrid MNPs. Results showed that MNPs with longer PDMAEMA arms exhibited broader suitable pH range to form Pickering emulsion, but slower magnetic responsiveness. An optimized sample MNP3 with DP of PDMAEMA ca. 65 was screened out and tested to prove efficient separation of diesel emulsion droplets from water and the recyclability of the hybrid MNPs.

© 2014 Elsevier Ltd. All rights reserved.

1. Introduction

Core-shell structured inorganic/organic hybrid nanoparticles have attracted ever increasing attentions due to their fascinating properties and functions when combining both inorganic and organic compositions into one entity [1,2]. These hybrid nano-objects are often prepared using one of two strategies: a "grafting to" method [3–5] by tethering polymer chains onto the inorganic particles and a "grafting from" method [6–10] by growing polymer chains from the initiating sites on the particle surface. The polymeric shell in the hybrid materials not only protects the inorganic core from the environment and prevents particle aggregation [11–16], but also renders the materials novel properties, such as tunable surface polarity and stimuli-responsiveness toward environmental change [3,17–20].

Depending on the composition and length of the polymer arms, lots of hybrid nanoparticles show property of being able to assemble at the oil–water interface and therefore function as particulate stabilizers to form Pickering emulsions [21–25]. Although the formation of Pickering emulsion, such as the oil-in-

* Corresponding author. *E-mail address:* hgao@nd.edu (H. Gao).

http://dx.doi.org/10.1016/j.polymer.2014.12.056 0032-3861/© 2014 Elsevier Ltd. All rights reserved. water system, has been extensively reported using various types of polymeric and inorganic nanoparticles, such as silica nanoparticles [24,26,27], clays [28,29], microgels [24,30,31], and polymeric latexes [32,33], few studies have directly used hybrid nanoparticles with inorganic core and polymer shell to form Pickering emulsions [21,22,25,34].

Efficient separation of oil from produced water streams represents an important process in petroleum industry. Current practices in industry use either gravity separator [35] or metal mesh [36] to separate oil from water. However, the generated water effluent often contains micrometer-sized oil droplets dispersed in water, forming a stable oil-in-water emulsion even without any stabilizer [37]. Further reduction of oil content in this water effluent becomes fairly difficult and may cause significant concerns to environment and public health. To address this challenge, hybrid nanoparticles that contain a superparamagnetic core and a stimuli-responsive polymer shell become a desired solution since they can efficiently and reversibly adhere to the dispersed oil droplets in the emulsion [38–42]. When applying an external magnetic field, the interfaceadhered magnetic particles allow facile separation of oil droplets from the water phase. The superparamagnetic particles have negligible remnant magnetization avoids their aggregation, both during storage and after magnetic field treatment [16,43,44]. Meanwhile, the use of stimuli-responsive polymer (sensitive to



temperature, pH, electric fields etc.) as shell can break the concentrated Pickering emulsion after magnetic separation on demand, to finally recover the hybrid nanoparticles for a second round of separation. In addition, tethered polymeric materials on the MNPs give them antifouling properties and provide steric repulsion keeping particles apart from one another [16,45]. Recently, Schmidt et al. [39] reported the use of superparamagnetic nanoparticles coated with polystyrene arms as the stabilizers for the preparation of cyclohexane-in-water Pickering emulsions, which were easily destabilized under magnetic heating via AC magnetic field treatment. Richtering et al. [40] used Fe₃O₄@poly(Nisopropyl acrylamide) microgels that contained magnetic core and thermoresponsive polymer shell to alter the toluene-in-water emulsion stability under an oscillating magnetic field to separate oil from water. Peng et al. [41] reported the use of core-shell structured magnetic nanoparticles as magnetic separators to destabilize water-in-oil inverse emulsion and separate water from oil. However, to the best of our knowledge, no study so far has reported the use of pH and magnetic dual responsive nanoparticles as recyclable stabilizers for efficient oil-water separation.

In this contribution, we designed a core-shell structured hybrid magnetic nanoparticle (MNP) for effective separation of emulsified oil droplets (several to tens of microns in size) from water, which cannot be easily achieved using either gravity plate separator [46] or membrane techniques [36]. The hybrid MNPs contained a cluster of magnetic nanoparticles as the core and poly(2dimethylaminoethyl methacrylate) (PDMAEMA) as arm, showing dual stimuli-responsiveness to both external magnetic field and environmental pH. The sensitivity of polymer arms to pH could alter the surface polarity of the MNPs to reversibly form and break the oil-in-water Pickering emulsion. A complete cycle of the separation of emulsified oil from water is illustrated in four steps (Scheme 1) when diesel was used as an example of the hydrophobic oils. An emulsion that contained 2.5 wt% of diesel droplets in water with no stabilizer showed high stability over weeks. In the first step, addition of an MNP stock solution into the emulsion under a proper pH allowed the adsorption of the MNPs to the diesel-water interface and formed a Pickering emulsion without altering the size of oil droplets. Second, applying an external magnetic field quickly dragged and concentrated the MNP-coated oil droplets from water and achieved a recovery of 90 wt% of water by decantation. Third, decreasing the water pH in the concentrated diesel-in-water

emulsion destabilized the oil droplets and separated the oil from the MNP-dispersed aqueous phase. In the last step, the MNP aqueous dispersion was recovered after separation from the diesel oil and reused in a second round of oil separation from water.

2. Results and discussion

2.1. Synthesis of the core-shell structured MNPs

Hybrid MNPs containing a cluster of superparamagnetic Fe₃O₄ nanoparticles as core, a thin layer of SiO₂ middle shell and a pHresponsive PDMAEMA outer shell were successfully synthesized in four steps, as illustrated in Scheme 2. First, magnetic clusters (termed as MP) containing lots of spherical superparamagnetic Fe₃O₄ nanoparticles with size around 20 nm (Fig. 2D) were synthesized using a solvothermal method according to the literature [47,48]. The produced MPs showing an average diameter of 112 nm in transmission electron microscopy (TEM) were then coated with a thin layer of silica to improve the stability of the MPs in dispersion. These produced MP@SiO₂-OH nanoparticles containing hydroxyl groups on the silica surface were subsequently modified using 3aminopropyltriethoxysilane (3-APTES) to make MP@SiO₂-NH₂ followed by reaction with 2-bromoisobutyryl bromide to introduce bromine initiating groups, producing MP@SiO₂-Br [49]. Finally, surface-initiated atom transfer radical polymerization (SI-ATRP) [6,46,50-54] of DMAEMA was applied to grow polymer shells. Samples were taken out of the reactor at timed intervals with different DMAEMA conversions to obtain a series of 6 MNPs with various PDMAEMA arm lengths. These MNPs are designated as MP@PDMAEMA_x, in which the subscript "x" represents the average degree of polymerization (DP) of the PDMAEMA arms in each sample: MP@PDMAEMA35, MP@PDMAEMA53, MP@PDMAEMA65, MP@PDMAEMA156, MP@PDMAEMA223 and MP@PDMAEMA288, which was determined in DMF size exclusion chromatography (SEC) based on linear poly(methyl methacrylate) (PMMA) standards after detaching the PDMAEMA arms from the MNPs. In the following discussion, these six hybrid MNPs are referred as MNP1, MNP2, MNP3, MNP4, MNP5 and MNP6, respectively (Table 1).

Fig. 1 shows representative TEM images of the bare MP (Fig. 1A), MP@SiO₂-OH (Fig. 1B) and MNP3 (MP@PDMAEMA₆₅) (Fig. 1C, D) nanoparticles. The hybrid MNP3 exhibited a layered structure with a spherical magnetic cluster core (~110 nm diameter), a SiO₂ middle



Scheme 1. Application of pH-responsive magnetic nanoparticles (MNPs) as recyclable stabilizers for oil-water separation



Scheme 2. Synthetic scheme of the hybrid MNPs.

layer (~15 nm thickness) and a PDMAEMA arm layer (~15 nm thickness). With the increase of DMAEMA conversions, the produced MNPs showed an increased hydrodynamic diameters ranging from $D_h = 157$ nm to 298 nm, determined by dynamic light scattering (DLS) in water under pH = 7 (Fig. 2A), indicating a successful synthesis of core-shell structured MNPs with tunable polymer arm lengths.

After using HF solution to etch the silica layer, the PDMAEMA arms were cut off from the hybrid MNPs for characterization of molecular weights using DMF SEC (Fig. 2B). All six PDMAEMA chains showed monomodal SEC chromatograms with narrow molecular weight distribution ($M_w/M_n = 1.2-1.3$). The molecular weights of polymer arms increased linearly with DMAEMA conversions (Figure S1 in the SI), suggesting well-defined arm structures in controlled syntheses.

Fig. 2C shows the thermo-gravimetric analysis (TGA) results of hybrid nanoparticles. Before surface polymerization, there exists ~0.4 wt% difference in the weight retentions at 800 °C between amino- and 2-bromoisobutyrate-functionalized silica nanoparticles (Fig. 2C), which represents the weight fraction of organic initiating groups in the MP@SiO₂—Br. After SI-ATRP of DMAEMA, significant weight loss of each MNP sample was observed in the TGA analysis, indicating the successful incorporation of PDMAEMA hairs on the MNPs. The contents of polymer fractions were summarized in Table 1. With the varied arm lengths, the weight losses of the hybrid MNPs in the TGA analysis varied from 4% in sample MNP1 to 20% in MNP6. Thus, there were averagely $1.7-1.9 \times 10^4$ PDMAEMA chains per silica coated magnetic nanoparticle and the polymer grafting density was around 0.3 chain/nm² (detailed calculation in SI).

Properties of core-shell structured MNPs. Magnetic property is one of the key features of the hybrid MNPs. To separate the emulsified oil droplets and recycle the hybrid MNPs, it is important that the hybrid MNPs are superparamagnetic with fast response to external magnetic field. The magnetic properties of bare MPs, MP@SiO₂-Br and the series of PDMAEMA-coated MNPs were determined using a superconducting quantum interference device (SQUID) magnetometer and the results are shown in Fig. 2D with saturation magnetization values summarized in Table 1. All samples

Table 1				
Physical	properties	of hy	vbrid	MNPs.

exhibited no hysteresis of magnetism, indicating that the core was a cluster of superparamagnetic nanoparticles with size smaller than 30 nm [48,55,56]. The bare MP showed a saturation magnetization of 85 emu/g and this value decreased with the incorporation of silica shell and PDMAEMA polymer arms. All hybrid MNPs showed magnetic responsiveness and could be effectively concentrated from their aqueous dispersions when using a magnet, as shown in the inset of Fig. 2D.

The length of PDMAEMA arms determines the pH-responsiveness of the MNPs. In general, the polymers tethered on a particle surface often show a hysteresis in transition from hydrated to dehydrated states when responding to environmental change [57]. For instance, upon the increase of environmental pH, the surface hydrated PDMAEMA segments would deprotonate first to form a thin dehydrated layer and thus slow down the inner polymer's responsiveness. This phenomenon becomes more significant in MNP samples with longer polymer arms, which are expected to show a broader pH range in transition than MNPs with shorter PDMAEMA arms when increasing the environmental pH. The hydrodynamic sizes and zeta potentials of these six hybrid MNPs at different pH values were tracked by DLS equipped with an autotitrator. In Fig. 3, all hybrid MNPs show a decreased hydrodynamic size with increased pH. When the environmental pH was around 7.1–7.2, close to the apparent pKa of linear PDMAEMA in water [58–60], a sharp decrease of hydrodynamic size was observed in all MNP samples, although the transition finished at various pH values, depending on the PDMAEMA arm lengths.

The transition of PDMAEMA arms from protonated state to deprotonated state with the increase of environmental pH was confirmed by the physical appearance of these aqueous dispersions, switching from low pH (well dispersed) to high pH (precipitates) as shown in the inset of Fig. 3B. The titration of MNPs with different PDMAEMA arm lengths revealed a suitable pH range for each hybrid MNP, in which the PDMAEMA arms showed amphiphilic nature with partial protonation of the tertiary amine groups and overall positive zeta potential. It is expected that an MNP within this pH range can assemble at the oil—water interface within a short period of treatment time.

	DP ^a	$M_{n,RI}{}^a~(\times 10^3)$	M_w/M_n^{a}	D _h ^b (nm)	CV ^b	Polymer content ^c (wt%)	No. of polymer per MNP ^d (×10 ⁴)	Magnetic saturation value ^e (emu/g)
Bare MPs	N/A	N/A	N/A	130	0.25	0	N/A	85.2
MP@SiO2-Br	N/A	N/A	N/A	143	0.23	0	N/A	79.5
MNP1	35	5.4	1.29	157	0.21	4.0	1.9	77.1
MNP2	53	8.1	1.29	163	0.19	5.2	1.9	75.9
MNP3	65	10.2	1.30	179	0.17	6.3	1.9	75.1
MNP4	156	24.5	1.32	225	0.16	11.6	1.8	70.5
MNP5	223	35.1	1.33	267	0.19	15.1	1.7	66.7
MNP6	288	45.2	1.34	298	0.20	20.0	1.7	63.4

^a Degree of polymerization (DP), apparent number-average molecular weight (M_{n,Rl}) and molecular weight distribution (M_w/M_n) measured by DMF SEC with RI detector, calibrated with linear PMMA standards.

^b Hydrodynamic diameter (D_h) and coefficient of variation (CV) of bare MPs (in acetone), MP@SiO₂-Br (in acetone) and MNPs (in pH = 7 water) were measured by DLS. ^c Polymer weight fraction measured by TGA under N₂ at a heating rate of 10 °C/min.

^d See SI for detailed calculation.

^e Magnetic property characterized using an MPMS® SQUID system (Quantum Design, San Diego, CA).



Fig. 1. (A) TEM images of bare MP, (B) MP@SiO₂-OH, (C) MNP3 (MP@PDMAEMA₆₅), and (D) a zoom-in image of MNP3.



Fig. 2. A) Hydrodynamic diameter of hybrid MNPs in water under pH 7. B) SEC traces of the detached PDMAEMA arms based on linear PMMA standards in DMF. C) TGA curves of the MP@SiO₂-NH₂, MP@SiO₂-Br and the hybrid MNPs with various polymer arm lengths. D) The magnetic hysteresis loops of bare MP, MP@SiO₂-Br and the hybrid MNPs with inset of digital pictures to show the magnetic responsiveness after dispersed in water.



Fig. 3. Evolution of hydrodynamic diameter (A) and zeta potential (B) of the MNPs as a function of environmental pH. All MNPs aqueous dispersions with initial pH = 2 were titrated using 0.01 M NaOH solution. The digital pictures in B inset show the physical appearance of the dispersions of MNP3 at pH < 7 and >10 at 25 °C.

2.2. The pH and magnetic responsiveness of MNP-coated Pickering emulsion

To confirm the suitability of the pH range for each MNP sample, all six MNPs (in aqueous stock dispersion with concentration of 0.4 g/mL) were tested to form diesel-in-water Pickering emulsion (2.5 wt% of diesel-in-water with 5 wt% of MNP to diesel) under different pH values. For example, MNP3 as the stabilizer was able to form stable diesel-in-water Pickering emulsions at any pH within the range from 7.1 to 8.5 (Fig. 4) when the PDMAEMA arms in the MNP were partially protonated with a positive zeta potential (34.5–2.7 mV) and showed an amphiphilic surface property. Beyond this pH window, the MNP surface would be either too hydrophilic at lower pH or too hydrophobic at higher pH, thus couldn't stabilize the diesel droplets in water. Correspondingly, the diesel and water mixture was in a bilayer appearance at pH < 7.0 and pH > 8.5 (Fig. 4). Inset is the digital pictures showing the appearances of the diesel/water mixtures under different pHs.

To determine the magnetic responsiveness, each MNP at the optimized pH environment was used to form a 3 mL diesel-inwater emulsion in a 4 mL scintillation vial. Upon exposure to a magnet, the MNP-coated diesel droplets showed instantaneous response with unidirectional movement toward the vial wall as demonstrated in Video 1 recorded by a digital camera. By using an optical microscope equipped with a CCD camera, the response of diesel droplets to the magnetic field was recorded in Video 2. The



Fig. 4. Illustration of the effect of pH on the formation of diesel-in-water Pickering emulsion using MNP3 as stabilzier. Inset includes digital pictures of the diesel-in-water at various pHs.

time required to complete this separation for each Pickering emulsion was used to compare the magnetic responsiveness of the MNPs (Table 2). The magnetic responsiveness time decreased with the increased PDMAEMA arm length in the MNPs, in agreement to the trend of magnetic saturation values of the samples. The results in Table 2 demonstrate the trend that a MNP with longer arms exhibited a broader pH range suitable of forming Pickering emulsions, but slower magnetic responsiveness. The MNP1 with PDMAEMA₃₅ arms had the narrowest pH range of 0.4 (from 7.1 to 7.5), while the MNP6 with the longest PDMAEMA₂₈₈ arms had the broadest pH range of 2.3 (from 7.1 to 9.4). On the other hand, the time needed to remove the diesel droplets increased from 22 s using MNP1 to 102 s using MNP6. It is evident that there is a need to balance the effect of PDMAEMA arm length on these two counteracting properties and screen out the optimal sample for further study of diesel-water separation. Fig. 5 shows the arm length effect on both pH range and magnetic responsiveness of the six MNP samples. The two curves crossed at DP = 90, representing an optimal PDMAEMA arm length with balanced effect. Of the six available hybrid MNPs. MNP3 with PDMAEMA arm of DP = 65. which was the closest value to the DP 90, was thus selected for further study.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.12.056.

The hybrid MNP3 demonstrated capacity to stabilize various hydrophobic oils in water and form stable Pickering emulsions. Fig. 6 shows the optical microscopy images of the three Pickering emulsions at pH = 8.1 by using three representative hydrophobic oils (diesel from gas pump, aromatic anisole and aliphatic *n*-dodecane). All these Pickering emulsions were stable for at least 1

Table 2
Effect of arm length on the pH and magnetic responsiveness of hybrid MNPs.

	pH range ^a	Zeta potential range ^b	pH of measurement ^c	Magnetic responsiveness ^d (sec)
MNP1 MNP2 MNP3 MNP4 MNP5 MNP6	7.1–7.6 7.2–8.0 7.2–8.5 7.1–9.1 7.1–9.3	32.4–3.5 33.3–2.8 34.5–2.7 35.2–2.8 36.0–3.1	7.3 7.6 8.1 8.5 8.9	21 27 42 73 91
101111	7.1 5.1	57.2 5.5	5.0	102

^a The pH range, within which, MNPs could stabilize Pickering emulsion.

^b The zeta potential of each MNP with the listed pH range.

^c The pH value at which the MNP formed the most stable Pickering emulsion with minimal MNP in aqueous phase or precipitated out.

^d Time needed for MNP-coated diesel droplets to arrive to the scintillation vial wall.



Fig. 5. The effect of PDMAEMA arm DP on the pH range and magnetic responsiveness of each MNP.

month without any coalescence based on visual observation of the samples that showed no change on physical appurtenance change and no presence of aggregates. At the same time, increasing and decreasing the environmental pH across the suitable pH window can quickly form and break the Pickering emulsions. For instance, at pH 4, MNP3 couldn't stabilize the diesel-water mixture with 1:1 volume ratio (totally 3 mL) to form the Pickering emulsion. Addition of 25 µL of 0.1 M of NaOH solution changed the pH to 7.9 and the mixture quickly formed Pickering emulsion after gentle shaking, showing stable oil droplets with average size of 149 µm. Further addition of 25 μ L of 0.1 M of HCl solution into the stable diesel-in-water Pickering emulsion decreased the pH to 3 (out of the suitable window) and immediately destabilized the emulsion to form a bilayer mixture (Fig. 7 and Video 3 in SI). The property of the MNP3 to fast form and break the diesel-in-water Pickering emulsion by simply tuning the pH is critical to achieve the recyclability of the hybrid MNPs in the oil-water separation.

Supplementary video related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.12.056.

2.3. Application of MNP3 for separation of emulsified diesel droplets from water

A 3 mL diesel-in-water stock emulsion containing 2.5% of diesel by volume was made from powerful sonication. The emulsion without any stabilizer was stable over 3 weeks without significant phase separation, representing a realistic analog of the water effluent after gravity plate separation. Optical microscopy image of the diesel droplets before treatment with hybrid MNP3 in Fig. 8 reveals numerous emulsified diesel droplets with size less than 10 μ m. After addition of 10 μ L stock dispersion of MNP3 in water (concentration 0.4 g/mL) with pH = 8.1, the emulsion was still



Fig. 7. Reversible breaking and forming Pickering emulsion by tuning pH: a) a bilayer diesel-water mixture at pH = 4 since all hybrid MNPs were hydrophilic and stayed in water; b) addition of 25 μ L 0.1 M NaOH solution changed the pH to 7.9 and Pickering emulsion formed; c) further addition of 25 μ L 0.1 M HCl solution changed the pH to 3 and broke the Pickering emulsion.

homogenous with no evident change of the droplet size (Fig. 8). Upon applying an external magnetic field, the MNP-coated diesel droplets were removed to the vial wall and produced a continuous water phase. The water after this treatment was transparent and colorless (Fig. 8), which could be easily separated from the concentrated diesel oil and collected by decantation. Addition of HCl solution (0.1 M) into the concentrated MNP-coated diesel droplets destabilized the emulsion and produced a bilayer mixture with diesel on top of the MNP-dispersed aqueous phase. After decanting the oil out of the vial, the collected MNP dispersion was further treated with 0.1 M NaOH solution to tune the pH back to 8.1 before added to a second batch of diesel-water emulsion for separation. This recycling procedure was conducted for six rounds with no change in MNP morphology and oil separation efficiency. Fig. 8 shows the six batches of clear water after separation of oils by using the same batch of hybrid MNPs. The hybrid MNPs have high recyclability and can be used to purify the diesel-containing water at least six rounds without losing efficiency demonstrated by the absence of oil droplets in all optical microscopy images of the isolated water (Figure S4).

3. Conclusions

Well-defined hybrid MNPs that contained a magnetic cluster as core and densely grafted pH-responsive polymers as shell were used as recyclable stabilizers for oil—water separation. The magnetic core was synthesized via solvothermal hydrolysis of Fe(II) and Fe(III) salts in basic condition, and the surface-tethered PDMAEMA arms were produced via SI-ATRP of tertiary amine-containing DMAEMA. This rational design of dual responsive MNPs allowed the separation of MNP-coated oil droplets from aqueous phase when applying external magnetic field. At the same time, the pHresponsive polymer arms could change polarity upon environmental pH, thus reversibly form and break the Pickering emulsion



Fig. 6. Optical microscope images of 3 types of oil-in-water Pickering emulsion by using MNP3 as stabilizer. The ratios of oil to water were 1:1 by volume with 1 wt% of MNP3 to oil. The average sizes of oil droplets in the three Pickering emulsions were 149 µm, 85 µm and 56 µm, respectively.



Fig. 8. Demonstration of the recyclable application of hybrid MNP3 in isolation of diesel droplets from prepared stock diesel/water emulsion. The first row is the microscope images of the liquid in the scintillation vials in each step, the scale bar applies to all of the three pictures; the second row includes the digital pictures of the liquid appearances and the third row shows the digital pictures of the isolated water from different batches of diesel-containing water by recycling the same batch of MNP3.

as demands to recover the MNPs. The produced hybrid MNPs had a uniform size and the polymer hair lengths could be easily varied depending on the conversions of DMAEMA monomer during the SI-ATRP. Results indicated that MNPs with longer polymer arms showed broader pH windows suitable for forming Pickering emulsion, but slower magnetic responsiveness. Overall, an optimized MNP sample MNP3 that contained PDMAEMA arms with average DP = 65 was screened out and tested to prove efficient separation of diesel emulsion droplets from water. The same batch of MNPs could be recycled and used for six times without losing the particle morphology and separation efficiency. It is expected that the development of this novel hybrid MNPs with dual responsiveness can offer a facile and environmentally friendly route for the treatment of oil contaminated water.

Acknowledgments

The authors thank the University of Notre Dame, the Center for Sustainable Energy at Notre Dame and ACS Petroleum Research Fund (PRF #54298-DN17) for financial support. X.W. acknowledges the assistance from Han Xia and Professor Joan Brennecke for the TGA analysis. H.G. thanks the Support of Senior Visiting Scholar Foundation of Key Laboratory in Fudan University, China.

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.polymer.2014.12.056.

References

- [1] Caruso F. Adv Mater 2001;13(1):11-22.
- [2] Daniel M-C, Astruc D. Chem Rev 2003;104(1):293–346.
- [3] Zhu M-Q, Wang L-Q, Exarhos GJ, Li ADQ, J Am Chem Soc 2004;126(9):2656–7.
- [4] Lindenblatt G, Schärtl W, Pakula T, Schmidt M. Macromolecules 2000;33(25): 9340–7.
- [5] Iha RK, Wooley KL, Nyström AM, Burke DJ, Kade MJ, Hawker CJ. Chem Rev 2009;109(11):5620-86.

- [6] Pyun J, Kowalewski T, Matyjaszewski K. Macromol Rapid Comm 2003;24(18): 1043–59.
- [7] Sill K, Emrick T. Chem Mater 2004;16(7):1240–3.
- [8] Mandal TK, Fleming MS, Walt DR. Nano Lett 2002;2(1):3-7.
- [9] Vestal CR, Zhang ZJ. J Am Chem Soc 2002;124(48):14312-3.
- [10] Saha S, Bruening ML, Baker GL. ACS Appl Mater Interfaces 2011;3(8):3042-8.
 [11] Lutz J-F, Stiller S, Hoth A, Kaufner L, Pison U, Cartier R. Biomacromolecules
- 2006;7(11):3132–8. [12] Gillich T, Acikgöz C, Isa L, Schlüter AD, Spencer ND, Textor M. ACS Nano
- 2012;7(1):316–29. [13] Liu B, Zhang W, Yang F, Feng H, Yang X. | Phys Chem C 2011;115(32):
- 15875–84.
- [14] Zhelev Z, Ohba H, Bakalova R. J Am Chem Soc 2006;128(19):6324–5.
- [15] Amstad E, Gillich T, Bilecka I, Textor M, Reimhult E. Nano Lett 2009;9(12): 4042-8
- [16] Reddy LH, Arias JL, Nicolas J, Couvreur P. Chem Rev 2012;112(11):5818–78.
 [17] Perruchot C, Khan MA, Kamitsi A, Armes SP, von Werne T, Patten TE, Langmuir
- 2001;17(15):4479–81.
- [18] Chen X, Randall DP, Perruchot C, Watts JF, Patten TE, von Werne T, et al. J Colloid Interface Sci 2003;257(1):56–64.
- [19] Li D, Sheng X, Zhao B. J Am Chem Soc 2005;127(17):6248-56.
- [20] Durand-Gasselin Cl, Capelot M, Sanson N, Lequeux N. Langmuir 2010;26(14): 12321-9.
- [21] Saigal T, Dong H, Matyjaszewski K, Tilton RD. Langmuir 2010;26(19): 15200-9.
- [22] Saleh N, Sarbu T, Sirk K, Lowry GV, Matyjaszewski K, Tilton RD. Langmuir 2005;21(22):9873-8.
- [23] Fujii S, Armes SP, Binks BP, Murakami R. Langmuir 2006;22(16):6818-25.
- [24] Fujii S, Read ES, Binks BP, Armes SP. Adv Mater 2005;17(8):1014-8.
- [25] Motornov M, Sheparovych R, Lupitskyy R, MacWilliams E, Hoy O, Luzinov I, et al. Adv Funct Mater 2007;17(14):2307–14.
- [26] Binks BP, Lumsdon SO. Langmuir 2000;16(6):2539-47.
- [27] Binks BP, Philip J, Rodrigues JA. Langmuir 2005;21(8):3296–302.
- [28] Zhang J, Li L, Wang J, Xu J, Sun D. Langmuir 2013;29(12):3889-94.
- [29] Williams M, Armes SP, York DW. Langmuir 2011;28(2):1142-8.
- [30] Richtering W. Langmuir 2012;28(50):17218–29.
- 31] Ngai T, Auweter H, Behrens SH. Macromolecules 2006;39(23):8171-7.
- [32] Amalvy JI, Armes SP, Binks BP, Rodrigues JA, Unali GF. Chem Commun 2003;(15):1826–7.
- [33] Read ES, Fujii S, Amalvy JI, Randall DP, Armes SP. Langmuir 2004;20(18): 7422–9.
- [34] Saleh N, Phenrat T, Sirk K, Dufour B, Ok J, Sarbu T, et al. Nano Lett 2005;5(12): 2489–94
- [35] Cheryan M, Rajagopalan N. J Membr Sci 1998;151(1):13-28.
- [36] Jing B, Wang H, Lin K-Y, McGinn PJ, Na C, Zhu Y. Polymer 2013;54(21): 5771-8.
- [37] Fakhru'l-Razi A, Pendashteh A, Abdullah LC, Biak DRA, Madaeni SS, Abidin ZZ. J Hazard Mater 2009;170(2–3):530–51.
- [38] Melle S, Lask M, Fuller GG. Langmuir 2005;21(6):2158-62.
- [39] Kaiser A, Liu T, Richtering W, Schmidt AM. Langmuir 2009;25(13):7335–41.
- [40] Brugger B, Richtering W. Adv Mater 2007;19(19):2973-8.
- [41] Peng J, Liu Q, Xu Z, Masliyah J. Adv Funct Mater 2012;22(8):1732-40.
- [42] Peng J, Liu Q, Xu Z, Masliyah J. Energy Fuels 2011;26(5):2705-10.
 [43] Corot C, Robert P, Idée J-M, Port M. Adv Drug Deliv Rev 2006;58(14):
- 1471–504.[44] Neuberger T, Schöpf B, Hofmann H, Hofmann M, von Rechenberg B. J Magn Magn Mater 2005;293(1):483–96.
- [45] Durán JDG, Arias JL, Gallardo V, Delgado AV. J Pharm Sci 2008;97(8):2948-83.
- [46] Tsujii KO Yoshinobu, Yamamoto Shinpei, Goto Atsushi, Fukuda Takeshi. Adv Polym Sci 2006;197:1–45.
- [47] Liu J, Sun Z, Deng Y, Zou Y, Li C, Guo X, et al. Angew Chem 2009;48(32): 5875–9.
- [48] Guo J, Yang W, Wang C. Adv Mater 2013;25(37):5196–214.
- [49] Wu T, Zhang Y, Wang X, Liu S. Chem Mater 2007;20(1):101-9.
- [50] Tsujii Y, Ohno K, Yamamoto S, Goto A, Fukuda T. Surface-Initiated Polymerization I. Adv Polym Sci 2006;197:1–45.
- [51] Ejaz M, Yamamoto S, Ohno K, Tsujii Y, Fukuda T. Macromolecules 1998;31(17):5934-6.
- [52] Huang X, Wirth MJ. Anal Chem 1997;69(22):4577-80.
- [53] Hui CM, Pietrasik J, Schmitt M, Mahoney C, Choi J, Bockstaller MR, et al. Chem Mater 2013;26(1):745–62.
- [54] Matyjaszewski K, Miller PJ, Shukla N, Immaraporn B, Gelman A, Luokala BB, et al. Macromolecules 1999;32(26):8716–24.
- [55] Baumgartner Jens, B L, Widdrat Marc, Hirt Ann M, Faivr Damien. PLos One 2013;8(3):e57070.
- [56] Matthew Ferguson R, M KR, Khandhar Amit P, Krishnana Kannan M. Med Phys 2011;38(3):1619–26.
- [57] Stuart MAC, Huck WTS, Genzer J, Muller M, Ober C, Stamm M, et al. Nat Mater 2010;9(2):101–13.
- [58] Majewski AP, Stahlschmidt U, Jérôme V, Freitag R, Müller AHE, Schmalz H. Biomacromolecules 2013;14(9):3081–90.
- [59] Gohy J-F, Antoun S, Jérôme R. Macromolecules 2001;34(21):7435-40.
- [60] Rinkenauer AC, Schallon A, Günther U, Wagner M, Betthausen E, Schubert US, et al. ACS Nano 2013;7(11):9621–31.