Cationic Microgel Emulsion with a High Solid Content by a Multistep Addition Method in Inverse Microemulsion Polymerization

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ABSTRACT: The multistep addition of a monomer and initiator was developed to successfully synthesize cationic polyacrylamide microgels with solid contents (SCs) greater than 35% and cationic monomer concentrations of 0–40 mol % by inverse microemulsion polymerization. Two feed methods, three-step nonuniform addition and five-step uniform addition, were implemented to obtain microgel emulsions with 37% SC. The former addition method was designed according to the solubilization limit of the microemulsion before step polymerization, and that of the latter was a constant based on the remaining surfactant weight in the reactor. The product properties in the intermediate processes of these two methods were compared by dynamic light scattering and viscosity measurement. The results show that the products here were translucent microemulsions instead of milky ones when they were synthesized by a semicontinuous polymerization. Also, the particle sizes of these two methods were almost the same; this indicated that the oscillation phenomenon in continuous polymerization at a high SC was avoided. With the former feed method, the risk and operation cost in the synthesis process could be cut down greatly. Moreover, the viscosity of the cationic microgel emulsion conformed to the Krieger–Dougherty equation with a greater value of intrinsic viscosity than that of a hard-sphere system because of an electroviscous effect. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40585.

INTRODUCTION

In the oil and gas industry, microgels are used to modify profile of water injection to enhance oil recovery by a mechanism in which it can expand to tens of times of its original size by the absorption of formation water at the reservoir temperature so the water-dominant pores can be blocked. Afterward, the subsequent water can be diverted to unswept zones to displace more oil.[1] This method has been practiced with more than 85 treatments since the first application in Minas Field, Indonesia. Several successful cases have been reported.[2,3] In these applications, this microgel emulsion is usually synthesized by inverse microemulsion polymerization and with solid contents (SCs) of less than 32%.[1–3] An increase in SC decreases the surfactant usage per unit emulsion volume and alleviates the emulsification between the produced oil and water.

For decades, most studies that have aimed to increase the ratio of monomer to surfactant have focused on oil-soluble monomers, such as styrene and methyl methacrylate. The processes have included mainly multistep addition,[4–6] precursor emulsions polymerization,[7] semicontinuous feeding,[8–10] differential feeding,[11–14] Winsor I-like methods,[15] and the two-stage addition of the surfactant.[16] However, these methods are rarely applicable in the inverse microemulsion polymerization of acrylamide (AM) solution because of the distinctly different properties of the monomer, dispersed phase, and surfactant.

On inverse microemulsion polymerization, Candau and coworkers[17–20] have made lots of pioneering contributions, including the kinetic characterization and optimization of a formula with a cohesive energy ratio concept. To obtain a high-SC product with less surfactant, Hernández-Barajas and Hunkeler[21] proposed a hybrid heterophase water-in-oil polymerization, by which they obtained a 20% polymer emulsion with 8% surfactant usage. Subsequently, Ochoa and his coworkers[22–24] devoted much effort to the copolymerization of AM and [2-(acryloyloxy)ethyl]trimethylammonium chloride (ADQUAT) by semicontinuous and continuous processes. They obtained an inverse emulsion of lattices in the milky state with a high comonomer concentration of 30–42 wt % for 80/20 wt % ADQUAT/AM and the other comonomer concentration of 28–34.5 wt % for 60/40 wt % ADQUAT/AM. However, a high-solid latex with a lower cationic monomer content has rarely been reported

Table I. Synthesis Procedures of the Nonuniform Three-Step Addition Method

Procedure code	Oil content (g)	Water feed (g)[a]	Surfactant content (g)	Product amount (g)	Takeout (g)	SC (%)
3(1)	42	36 (36.66)	14	92	46	24.60
3(2)	21	14 (17.10)	7	60	30	33.60
3(3)	10.5	4 (9.20)	3.5	34	34	37.05

[a] The numbers in parentheses are the solubilization values on the phase boundary for each step.

because the high enthalpy of AM polymerization (81.5 kJ/mol) increases the difficulty of experimental control. In addition, the expenditure of a cationic monomer is quite high; thus, it is necessary to explore a practical method to deal with this problem.

Twenty years ago, Candau et al.[18] found that in the final microgel emulsion, there were two kinds of particles, narrowly dispersed polymer particles (40 nm) and small micelles of sodium bis(2-ehtyl-hexyl) sulfosuccinate. Then, their evaluation showed that the microgels were stabilized by about only 20% sodium bis(2-ehtyl-hexyl) sulfosuccinate, and the rest of the surfactant existed in the form of small micelles (1.6 nm).[19] Full et al.[25] further confirmed this result by the evolution of the particle size from unimodal before polymerization to bimodal after polymerization in the direct microemulsion polymerization of styrene. Afterward, Rabelero et al.[5] and Sosa et al.[4] successfully synthesized a colloidal emulsion of polystyrene and poly(vinyl acetate) with high monomer-to-surfactant ratio by a multistep addition method. In their processes, the monomer was added nearly 10 times, and this greatly increased the operational risk. Even worse, the polymer molecular weight decreased with increasing addition times,[26] so this may not be conducive to industrial applications. For these reasons, it is important to cut down on the number of addition steps.

In this study, stable and translucent microgel emulsions with SCs greater than 35% and an extensive ratio of AM to methacryloxyethyl trimethyl ammonium chloride (DMC) were synthesized by the multistep addition of the monomer and initiator. Two addition methods were used separately: nonuniform three-step addition and uniform five-step addition. The step load of the first method was determined according to the solubilization limit of microemulsion, and that of the second method was done according to the conventional uniform addition used by Hermanson and Kaler.[6] Also, the optimal step number and corresponding differences of the produced emulsions were evaluated by a comparison of the product features of these two methods.

EXPERIMENTAL

Experimental Materials

AM (analytically pure) was recrystallized by chloroform, and a 78 wt % water solution of methylacryloxyethyl trimethyl ammonium chloride (New Chemical Materials Co., Ltd., Zibo Yili) was extracted by benzene. Methylene bisacrylamide as a crosslinker, ammonium persulfate (APS) and sodium sulfite (SDS) as redox initiators, and Span80 (sorbitan monooleate, chemically pure) and Tween60 (polyoxyethylene 20 sorbitan

monostearate, chemically pure) as emulsifiers were used without purification. The aqueous phase consisted of a 63 wt % comonomer solution with the demanded molar ratio of AM to DMC, 0.02% methylene bisacrylamide, and 36.98% deionized water (conductivity <5 μS/cm). Industrial white oil (Karamay Petrochemical Plant), with a boiling range between 150 and 300°C, was chosen as the continuous phase. Unless otherwise specified, all of these chemicals were supplied by Sinopharm Chemical Reagent Co., Ltd.

Nonuniform Three-Step Addition Synthesis

The aqueous phase with an AM/DMC ratio of 90/10 mol % was used as a typical example for synthesis in a nonuniform addition method and a uniform addition method. To determine the solubilization limit, this aqueous phase was dripped stepwise into the oil phase, which consisted of 3 g of white oil and 1 g of surfactant blend. After the mixture was shaken to form a uniform emulsion, it was placed in a 30°C water bath to observe the phase behavior. All of the microemulsion conductivity values detected were lower than 0.3 μS/cm. The solubilization values on the phase boundary of each step of the nonuniform addition method are shown in parentheses in Table I.

The specific synthesis procedures are shown in Table I. The amounts of surfactant and oil listed in procedure 3(1) were mixed in a four-necked, round-bottomed flask equipped with a stirrer, reflux condenser, thermometer, and nitrogen inlet, and the reactor was placed in a 30°C water bath. After the water phase was added to the reactor, the reaction mixture was stirred at 300 rpm for 10 min to prepare a microemulsion. After a 15-min nitrogen purge, the mixture was initiated with 0.01 g of APS/SDS and reacted for 1 h. Afterward, some product was taken out for analysis. Then, the predetermined amount of the water phase from procedure 3(2) was added to the reactor in one batch. This mixture was again stirred for 10 min to form a microemulsion and initiated with 0.01 g of APS/SDS and so on. The reaction was maintained for 1 h before the addition of the next monomer solution in each step. To achieve a high SC with less steps, the solubilization values of 3(1) and 3(2) were set close to those at the phase boundary, and only a little monomer was added in procedure 3(3) to retain the same SC with a uniform five-step synthesis.

To compute the volume fraction of the internal phase (Φ; surfactant and microgel) of the produced emulsion, the emulsion density was determined by a gravimetric method at 30°C. Φ and the microgel density were calculated by the following equations:

$$\phi = 1 - (W_o/\rho_o)/(W_e/\rho_e) \qquad (1)$$

Table II. Synthesis Procedures of the Uniform Five-Step Addition Method

Procedure code	Oil content (g)	Water addition (g)	Surfactant content (g)	Product amount (g)	Takeout (g)	SC (%)
5(1)	63	24	21	108	36	14.00
5(2)	42	16	14	88	22	22.91
5(3)	31.5	12	10.5	78	26	29.07
5(4)	21	8	7	60	30	33.60
5(5)	10.5	4	3.5	30	34	37.05

$$\rho_e = \rho_o \phi_o + \rho_s \phi_s + \rho_g \phi_g \qquad (2)$$

where W and ρ separately represent weight and the density. In addition, the subscripts s, o, g, and e refer to the mixed surfactant, white oil, microgel, and emulsion, respectively. ρ_s and ρ_o were 1.002 and 0.819 g/cm^3, respectively. The viscosity of white oil was 0.043mPa s.

Uniform Five-Step Addition Synthesis

The uniform five-step addition procedures are shown in Table II. The synthesis operation was basically the same as the nonuniform addition method. The difference between the former method and the latter was that the weight ratio of the remaining surfactant to the newly added aqueous phase was kept constant at 7:8. Also, the monomer and initiator were added five times instead of three times. This uniform addition method was an analogy to the constant feed load described by Hermanson and Kaler.[6] In their experiments, they added the monomer step by step without taking out product in each step, but here, the product in each step had to be taken out to satisfy the requirements for dynamic light scattering (DLS) and rheology analysis.

Product Characterization

Conversion Determination. The conversion of the comonomer was represented by the residual monomer rate, which was defined as the molar ratio of remaining AM and DMC to the total comonomer moles in the aqueous phase. The rate after each step was determined by the bromination titration method.[27]

Particle Size Analysis. The particle morphology was observed by transmission electron microscopy (TEM; JEM-2100UHR, Japanese Electronics Co.). The particle size and particle size distribution were measured at 30°C by a DLS method with a Mastersizer 3000 high-speed intelligent particle size analyzer (Malvern Instruments) in backscatterring mode and at an angle of 173° with a 633-nm laser light. Before analysis, the product emulsion was diluted 400 times by cyclohexane. For each sample, three tests were performed.

Shear Rheology. The emulsion rheology of different SCs was measured at 30°C by a Thermo-Fisher Haake MAR rheometer with a P35TiL cone rotor with a cone angle of 2°, a diameter of 35 mm, and a taper-disk space of 0.105 mm.

RESULTS AND DISCUSSION

Conversion of Each Step

The polymerization of AM and DMC in the inverse microemulsion initiated with APS/SDS at 30°C was fast. As shown in

Figure 1, the residual monomer rate was only 0.6–1.6% 1 h after each step; this indicated that the conversion of the monomer to the microgel was close to 98% after each addition. The polymerization almost finished completely before the next addition of monomer.

Microgel Morphology

Figure 2(a) shows a 37% SC of the cationic microgel emulsion with the nonuniform addition method (left) and uniform counterpart (right). Their transmittances were determined separately to be 54.3 and 49.8% at 546 nm by a model 754 ultraviolet and visible spectrophotometer (Shanghai Optical Instrument Plant). The product was in a translucent state instead of in a milky state when it was synthesized by the semicontinuous method.[24] Both products were stable after centrifugation at 6000 rpm for 30 min.

Figure 2(b) shows the TEM photo of the final product in the nonuniform addition method. As shown in Figure 2(b) the microgels were spherical and almost uniform with a mean diameter of about 67 nm; this was smaller than the hydrodynamic diameter of about 93 nm determined by DLS. This diameter difference was probably due to the volatilization of the aqueous phase in the TEM sample preparation process, which caused this particle size reduction.[20]
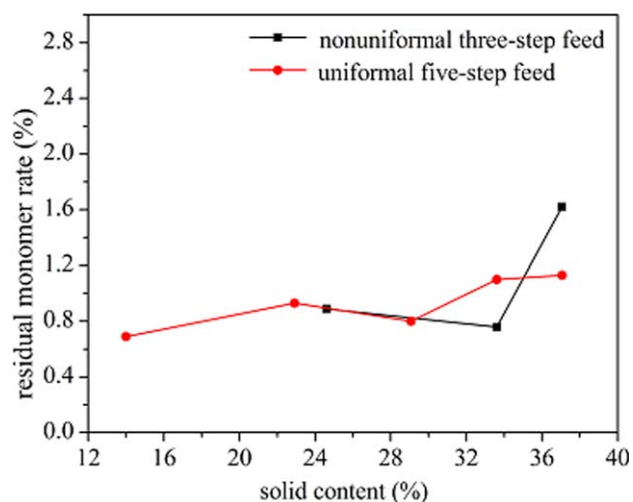

Figure 1. Evolution of the residual monomer values during the addition steps of the two methods. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
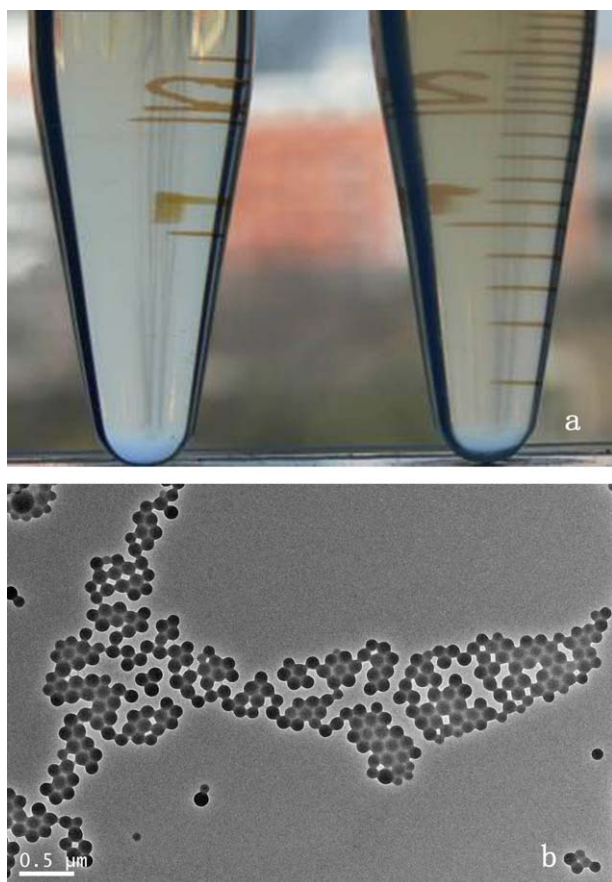
Figure 2. (a) Photograph of the microgel emulsion and (b) TEM photograph. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
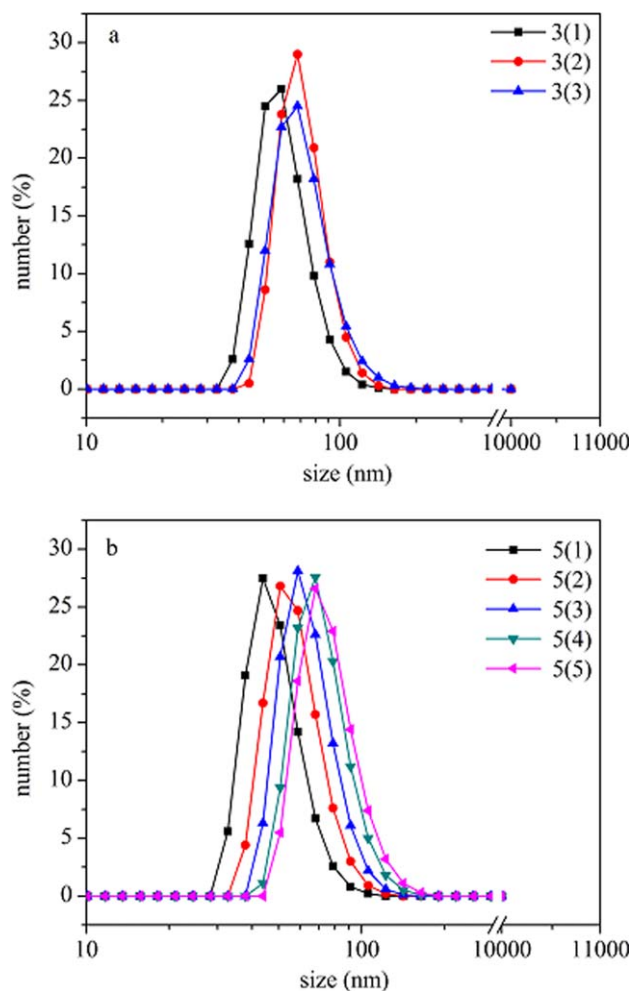

Figure 3. Particle size distribution changes with the procedures of the (a) nonuniform three-step addition method and (b) uniform five-step addition method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
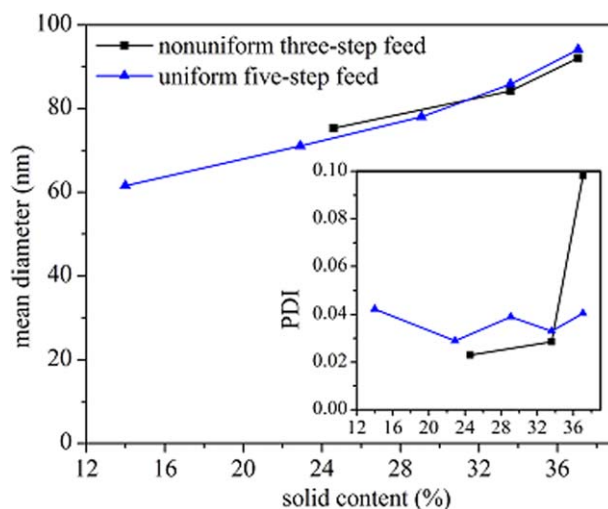
Size Distribution and Mean Diameter

According to the particle size distribution curves in Figure 3, the colloidal system corresponded with the normal distribution, and the particle size was in the range 30–200 nm. As the step advanced, the size peak shifted right, except in procedure 3(3), shown in Figure 3(a). Specifically for the uniform addition method shown in Figure 3(b), the closely paralleled curves indicated the uniform increment of particle size.

The variations of the z-average mean size and particle distribution index (PDI) with the SC of the steps are demonstrated in Figure 4. The mean particle sizes were nearly identical at the same SC for these two addition methods; this showed that the particle size oscillation in continuous addition could be avoided in the batch addition method.[28] The obvious difference was that the PDI of the final product of the nonuniform addition method suddenly widened up to 0.1; this was much larger than the 0.04 value of the uniform counterpart. In these systems, the polymerization took place in both swollen micelles initiated by the newly added initiator and particles where the residual initiator or active polymer radical initiated the monomer diffusing from swollen micelles.[16] This wider distribution showed that because of the lower feed of the initiator, secondary nucleation in the last step was more obvious in the nonuniform addition method than in the uniform counterpart.[10,16]

Figure 4. Changes in the z-average particle diameter and PDI (inset) with the SCs during the addition steps. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
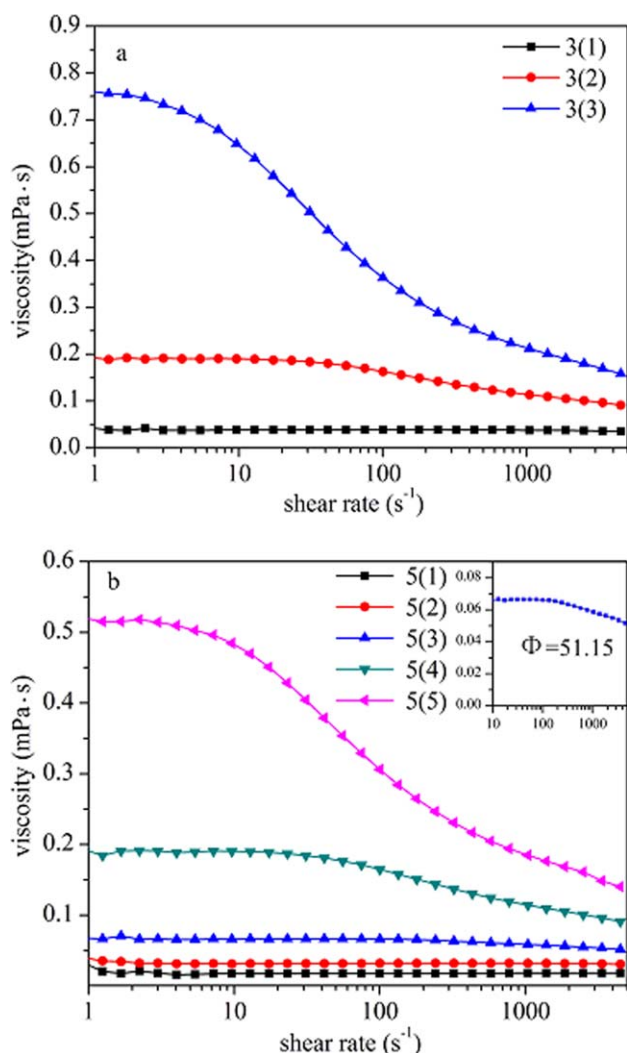
Table III. Physical Parameters of the Synthetic Products

Product code	ρ_e (g/cm^3)[a]	ρ_g (g/cm^3)[b]	Φ (%)[c]
3(1)	0.969	1.215	45.971
3(2)	1.016	1.211	56.591
3(3)	1.034	1.208	60.999
5(1)	0.916	1.202	34.754
5(2)	0.961	1.218	43.984
5(3)	0.991	1.209	51.154
5(4)	1.023	1.230	56.285
5(5)	1.031	1.200	61.137

[a] Density of the microgel emulsion.
[b] Density of the microgel.
[c] Volume fraction of the internal phase.

microstructure.[30] Additionally, the zero-shear viscosity of product 3(3) was higher than that of 5(5). This corresponded with a wider size distribution of 3(3), where a mass of small particles emerged and increased the viscosity, as is a feature of bimodal suspension systems.[31] Because the formed networks were destroyed at a high shear rate, the products of 3(2) and 5(4) or 3(3) and 5(5) had equally high shear limit viscosities of about a quarter of the zero-shear viscosity.

As shown in Figures 3–5 and Table III, the product parameters, such as the size, size distribution, and shear viscosities, in the two addition methods were almost the same when the SC was below 32%. Therefore, the addition numbers could be properly reduced according to the solubilization limits of the system so that both the operation cost and risk of synthesis decreased.

Figure 6 shows the relative viscosity (η_r) of the product changes with the volume fraction. The η_r–Φ curves fit well to Krieger–Dougherty equation [eq. (3)], which describes the rule for hard-sphere systems:[32]

Figure 5. Viscosity–shear rate curves of the products synthesized with the (a) nonuniform addition method and (b) uniform addition method. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Moreover, in a comparison of the curve slopes of the mean diameter versus SC, the diameter increment was found to be more significant than that of the stepwise polymerization of styrene[5] or hexyl methacrylate.[6] The reason was that all of the water-soluble initiators were apt to partition into the particles because of their insolubility in oil in inverse microemulsion polymerization,[29] whereas in direct microemulsion polymerization, they are apt to disperse into water to form new nucleation.

Shear Viscosity

The viscosity–shear rate curve and physical property parameters of the emulsions are shown in Figure 5 and Table III, respectively. As shown in Figure 5, the viscosity increased sharply as the steps advanced. The shear-thinning behavior occurred only at a Φ of 51.5%, as shown in the inset in Figure 5(b) and was close to the 50% value of the poly (methacryloxyethyl trimethyl ammonium chloride) (PDMC) microgel.[17] This shear-thinning behavior indicated the network formation of the particle
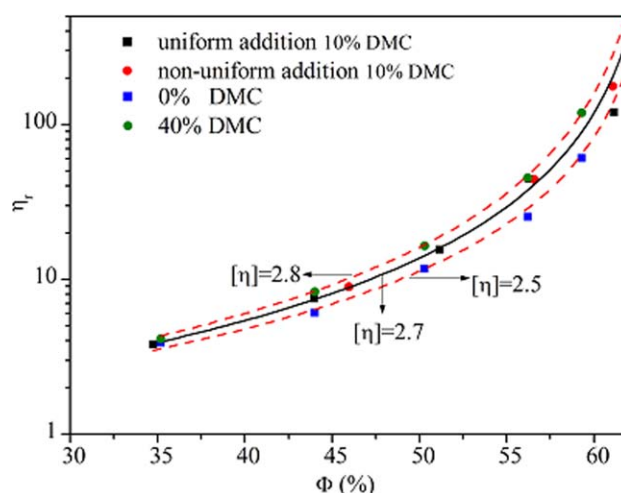

Figure 6. Test of the Krieger–Dougherty volume fraction equation fitted to the relationship between η_r and the volume fraction of the internal phase for the two addition methods and different DMC content systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

$$\eta/\eta_0 = \eta_r = (1 - \phi/\phi_M)^{-[\eta]\phi_M} \qquad (3)$$

where η and η_o are the apparent viscosities of the emulsion and oil, respectively; Φ_M represents the close-packing volume fraction (here, it was a random close-packing fraction of 63.7%); and $[\eta]$ is intrinsic viscosity, which is equal to 2.5 for hard-sphere suspensions. Here, for the best fit of eq. (3), $[\eta]$ was equal to 2.7. To explain this phenomenon, emulsions that consisted of 100%AM and 40/60 mol % DMC/AM were also synthesized. Both η_r–Φ curves conformed to the Krieger–Dougherty equation with η values of 2.5 and 2.8, respectively. $[\eta]$ agreed with that of the hard-sphere system at 0% DMC and increased with increasing DMC content. So, the reason for the greater $[\eta]$ of this cationic system compared to that of the hard-sphere system was probably an electroviscous effect[33] instead of the adsorption of organic solvent in the surfactant layer surrounding the particles.[17]

CONCLUSIONS

With the multistep addition of the monomer and initiator, cationic microgel emulsions with SCs greater than 35% and wider cationic monomer contents of 0–40 mol % were obtained via a batchlike addition process; this was simpler and more operable than semicontinuous or continuous processes in practical use. The nonuniform addition method, designed according to the solubilization limit after each step, could synthesize a microgel emulsion with a better transparency and higher viscosity. This feature is useful for designing the number of additions during the multistep addition microemulsion polymerization so that the operation costs and risks of synthesis could be reduced. In addition, the curve of η_r versus the volume fraction for this emulsion conformed to the Krieger–Dougherty equation, where $[\eta]$ was greater than that of the hard-sphere system because of an electroviscous effect.

ACKNOWLEDGMENTS

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