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FUNDAMENTAL PROPERTIES OF COLLOIDAL UNIMOLECULAR POLYMER PARTICLES

by

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A DISSERTATION

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PUBLICATION DISSERTATION OPTION

This dissertation has been prepared in the form of five papers for publication. Papers included are prepared as per the requirements of the journal in which they are submitted or will be submitted. Paper I, pages 18-51 has been submitted to Macromolecules. Paper II, pages 52-79 has been submitted to Colloid and Polymer Science. Paper III, pages 80-98 will be submitted to Langmuir. Paper IV, pages 99-115 will be submitted to Journal of Colloid and Interface Science. Paper V, pages 116-144 has been submitted to Journal of Coatings Technology: Research.

ABSTRACT

Colloidal Unimolecular Polymer (CUP) particles are a new genre of material formed by self-assembly into spheroidal particles due to the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent. The particle sizes were characterized by means of Dynamic Light Scattering with corrected viscosities instead of water's viscosity. The distribution of particle size agreed well with the distribution of molecular weight proving that the polymer had undergone unimolecular collapse. The rheology study shows the presence of surface water and its significant effect on the rheology. The primary and secondary electroviscous effects were also found to play roles when the suspension was in dilute to semi-dilute regime. When the volume fraction of particles were higher than 0.15, the rheology behavior fit well with Krieger-Dougherty equation. The thickness and the density of surface water were calculated to be 0.57nm and 1.0688 g/cm^3 respectively. When small amounts of external electrolytes were added, (<2% by weight), the viscosity of the suspensions (<0.06 by volume) dropped due to screening effect of the added electrolytes. When the volume fraction of the suspension increased or the addition of electrolytes increased, the viscosities of suspension increased sharply at different critical points. The CUPs showed remarkable surface activities, which increase with molecular weights. The calculated average equivalent area occupied by each particle was much smaller than that of the largest cross-section of the particle indicating that the liquid-solid interface contact angle of the particle was quite low, close to 10°.

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SECTION

1. INTRODUCTION

1.1 BACKGROUND

Polyelectrolytes are defined as macromolecules with many ionizable groups. In the last several decades, the transition of a flexible polyelectrolyte chain from a random-coil conformation or in fully extended state to a globular compact form in a collapsed state has been widely studied. The coil-globule transition of polyelectrolyte provides a simple fundamental model for various phenomena. Besides, its importance as a general and basic concept in polymer physics and solution dynamics has direct implications for many biological systems, such as protein folding, native DNA packing, and network collapse.

Due to the limitation of experiment techniques, the collapsed polyelectrolyte chains tend to aggregate and form precipitate from dispersing medium. Thus it is difficult to study the physical and chemical properties of collapsed polyelectrolyte chains. To find an easy way to prepare a stable suspension has been a difficult task for both polymer physical and chemical chemist.

One of the best methods is to prepare suspension of single isolated collapsed chains which are stabilized by charge repulsion or steric hindrance. The major challenge is the balance of hydrophilic/hydrophobic balance of polyelectrolyte. If the chains are too hydrophobic, then the collasped chains tend to aggregate. If the chains are too hydrophilic, the collapsed chains still remain chain-like conformation. Only at specific conditions when concentration of polyelectrolyte in solvent, temperature, pH, solubility of polymer in solvent and charge fraction of polyelectrolyte are coordinated properly, can the polyelectrolyte chains collapsed into a single isolated compact globule.

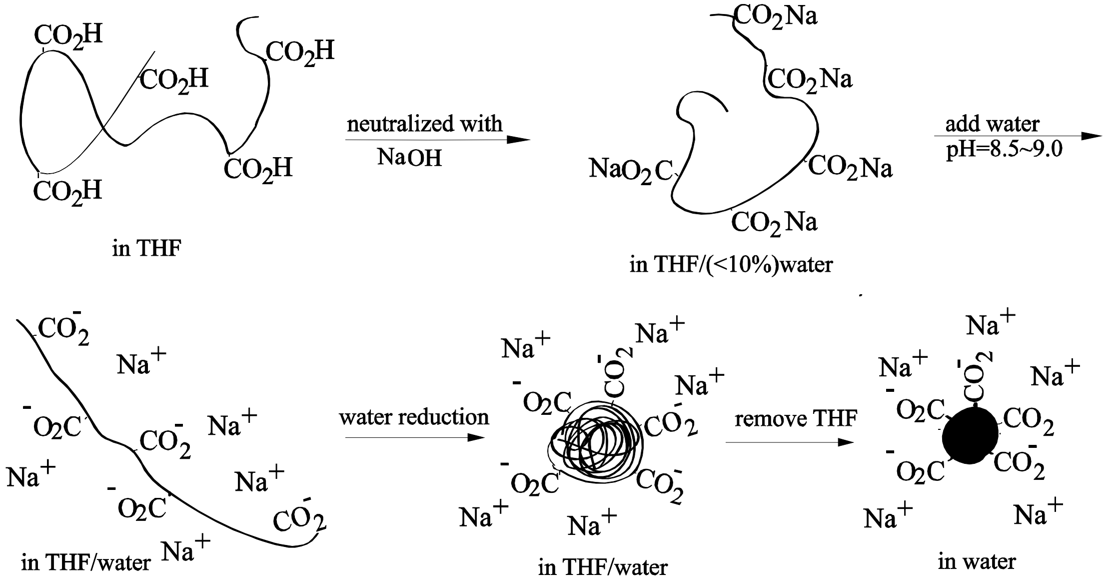
After numerous designing and synthesis, the stable collapsed polyelectrolyte chains has been finally successfully by Van De Mark's research group and has been named with colloidal unimolecular polymer (CUP).[1] Colloidal Unimolecular Polymer (CUP) particles are a new type of true nanoscale material.[1b] CUPs are formed by the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent.

The formation of CUP particles is driven by the polymer-polymer interaction being greater than the polymer-solvent interaction and entropically favored by release of the water analogously to micelle formation with hydrophilic or charged groups creating the sphere-like shape. Scheme 1.1 shows the formation of CUP particles with carboxylate groups on the surface, keeping the particles from aggregation. Once formed these colloidal particles are thermodynamically stable.[1a] The CUP suspension contains only charged particles, water and counterions.

Due to its specific structure, there are several advantages of CUPs being treated as model material to study biomacromolecules. First, CUP is formed by a single strand of polymer chain with ionization groups, which is close to the conformation of globular protein's. Second, CUPs is free of surfactant and the preparation procedure is quite simple while surface modified latex involves with tedious dialysis to remove the surfactant. Third, the size and charge density can be easily. Therefore, CUP is a very good model material to study the fundamental properties of protein or analogous particles.

In addition, as an innovative material, CUP can find its application area in coating, drug delivery, catalyst matrix, etc. Therefore, it is important to investigate the basic properties of CUP particles. This thesis majorly focus on the studies on colloid properties of CUP, including particle sizing, rheology, surface tension, and electrokinetic behaviors. The electrokinetic behavior will be covered here, and the rest will be addressed in the formal chapters in the thesis.

Scheme 1.1 Process of forming CUP particles from poly(methyl methacrylate-co-methacrylic acid).



As charged particles dispersed, in water which has high dielectric constant, CUPs are expected to have interesting electrokinetic behavior. Generally, there are four electrokinetic phenomena. They are electrophoresis, electroosmosis, streaming potential and sedimentation potential. Electrophoresis is the emphasis of this research since it refers to movement of a particle relative to stationary liquid under the influence of an applied electrical field. Electrophoresis is defined as the migration of charged colloidal particles or molecules through a solution under the influence of an applied electric field. The special sense of studying electrophoresis is that it is closely related to the rheological behavior of a suspension.

In terms of electrophoresis, the fundamental parameters are zeta potential, ζ, Debye-Hückel parameter, κ and electrophoretic mobility, μ. The zeta potential is the potential at the surface of shear which is defined as the layer of liquid immediately adjacent to a particle and moves with the same velocity as the surface. The precise boundary of surface of shear is unknown, but it is assumed to be within a couple of molecular diameters away from the surface of particle. For regular suspensions where the ionic strength is dominated by added electrolytes, the κ is expressed as follows:

$$\kappa^2 = [\left(\frac{e^2}{\epsilon k_B T}\right) \sum_i z_i{}^2 n_{i\infty}] \tag{1}$$

where e is elementary charge, ε is permittivity of the solvent, k_B is the Boltzmann constant, T is the temperature, z_i is the charge number of the electrolyte ions in the solution and $n_{i\infty}$ is the number of ions for each ion. The uint of κ^2 is m^{-2}, so κ^{-1} has the unit of meter. Another definition of κ is following the Debye- Hückel approximation,

$$\psi = \psi_0 \exp(-\kappa x) \tag{2}$$

where ψ_0 is the surface potential of particle, x is the distance from the particle surface and ψ_0 is the potential at surface, when $x = \kappa^{-1}$, $\psi = \psi_0/e$. Since κ^{-1} has the unit of meter, it is often called Debye length, and taken as the thickness of electrical double layer, which is strictly incorrect though they are comparable. Electrophoretic mobility is the velocity of an ion per unit electrical field with unit ms^{-1}/Vm^{-1} or $m^2V^{-1}s^{-1}$.

The relation between zeta potential, electrophoretic mobility and Debye-Hückel paprameter constitute the foundation of electrophoretic properties of CUP. If the surface potential is low enough to justify $\frac{e\psi}{k_BT} < 1$, and the ion atmosphere is undistorted by the external field, then[2]

$$\mu = \frac{2\epsilon\xi}{3\eta} f(\alpha) \tag{3a}$$

where α is the ratio of radius of particle to Debye length, i.e. α= κa, and

$$f(\alpha) = (1 + \frac{1}{16}\alpha^2 - \frac{5}{48}\alpha^3 - \frac{1}{96}\alpha^4 - \frac{1}{96}\alpha^5 - (\frac{1}{8}\alpha^4 - \frac{1}{96}\alpha^6)\exp(\alpha)\int_{\infty}^{\alpha}\frac{e^{-t}}{t}dt) \tag{3b}$$

with α <1. For α >1,

$$f(\alpha) = (\frac{3}{2} - \frac{9}{2}\alpha^{-1} + \frac{75}{2}\alpha^{-2} - 330\alpha^{-3}) \tag{3c}$$

The equations 3a, 3b and 3c are Henry's equation. On the base of the Henry equation, Oshima[3] corrected the factor $f(\alpha)$ to ζ[3], which is a good approximation up to $\frac{ze|\xi|}{k_BT} < 4$.

The above equations are applicable to particles with constant charge density. For the dilute regime, where the particle-particle interaction can be considered negligible, these equations work well. But when the concentration of particles increases, the distance between particles decreases. Consequently, the static electronic repulsion increases until at a critical point the counterion collapses on the surface of particles to decrease the charge density of surface so that the particles can further approach each other. These phenomena have been documented as counterion condensation[4].

For a deionized suspension like CUPs, the scenario will be even more complicated since the counterion comes from the dissociation of surface group of particles. As the concentration of CUP increases, the concentration of counterions also increase causing the Debye-Hückel parameter to increase, which indicate that the electrical double layer is compressed. Then the effective diameter of charge particle decreases, which counters the effect of counterion condensation.

Due to the complicate of the ionic and the electrokinetic environment, the average effective charges on each particle are difficult to calculate. The effective charge is a very important parameter in colloid behavior: it is related to rheology, surface tension, and stability. There are many methods to measure effective charges based on different models, and results from different methods can vary significantly. In this study, the measured conductivities and electrophoretic mobilities of CUP suspension with different volume fractions will be presented, and the effective charges will be calculated.

1.2 DETERMINATION OF EFFECTIVE CHARGE

1.2.1 Nernst-Einstein Model[5]. The immediate and simple relationship between the electrophoretic mobility, μ, and the friction coefficient, f, and the effective charge Q_{eff} is based on the assumption that the counterions surrounding the macro-ions have no interactions with the macro-ions and can be expressed as equation 4.

$$\mu = \frac{Q_{eff}}{f} \tag{4}$$

The friction coefficient, f, is related to the diffusion coefficient, D, by the Stokes-Einstein equation as equation 5, if the particle can be treated as a sphere with radius a where k_B is Boltzman constant, T is absolute temperature, η is viscosity of suspension medium.

$$D = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta a} \tag{5}$$

Combining equation 4 and 5, the relationship between electrophoretic mobility and effective charge can be expressed as equation 6 where μ^{∞} is electrophoretic mobility extrapolated to infinite dilution.

$$Q_{eff} = 6\pi\eta a\mu^{\infty} \tag{6}$$

The advantage of this model is its simplicity. As long as the electrophoretic mobility is at infinite dilution and particle size is known, then the effective charge can be determined. The major disadvantage is that there is no available model to extrapolate the μ^{∞} for spherical particles.

1.2.2 Hessinger's Model[6]. If a deionized suspension with low surface pKa is neutralized by a strong base like NaOH, the conductivity of the suspension and electrophoretic mobility of particle will change correspondingly. When all protons are neutralized, the relationship can be expressed as equation 7 where σ is the conductivity of suspension, n is the number density of particles, Z_{eff} is the effective charge, μ_p and μ_{Na^+} are electrophoretic mobilities of the particle and sodium ion respectively, M is the concentration of small ions per particle defined as $M=1000cN_A/n$ where c is the concentration of small ions in mol/L, σ_b is the conductivity of the background.

$$\sigma = ne[Z_{eff}(\mu_p + \mu_{Na^+}) + M(\mu_{OH^-} + \mu_{Na^+})] + \sigma_b \tag{7}$$

The effective charge can be determined from the dependence of conductivity on the number density of particles. This method is also relatively simple. The disadvantage is that it involves measuring the conductivity and electrophoretic mobility, which normally needs several instruments.

1.2.3 Charge Renormalization. The concept of charge renormalization was first raised by Manning[4] and was widely accepted in charge stabilized colloidal suspensions. The major idea is that some counterions surrounding macro-ions will bind or condense on the surface of macro-ion due to minimization of electro static repulsion between charges, which cause the effective charge to be smaller than the bare charge of the colloidal particle.

Alexander[7] et al. have done pioneering work on the calculation of the effective charge for spherically charged particles. The model is based on the assumption that each colloidal particle occupies the center of a spherical Wigner–Seitz (WS) cell[8] with the presence of counterions. Thus, the charge density profile can be readily calculated as well as effective charge. Alexander's model works well for colloidal particle with known bare charges. For a spherical particle containing weak acid or base groups on the surface, the bare charge is regulated by the dissociation equilibrium at the surface of the particle. Ninham and Parsegian[9] firstly proposed a model in which the surface of colloid contains ionizable groups which dissociates depend on the counterion atmosphere. The basic idea is that two electrical repulsive surfaces tend to minimize the total free energy. Based on that theory, Belloni[10] further developed a simple program to calculate the effective charge as long as the particle size, maximum bare charge, pKa, of the ionizable groups, pH of the reservoir solution, and salinity of reservoir are known.

1.2.4 Other Models or Methods. Other than the models mention above, there are also some other models to determine effective charge such as O'Brien-White-Oshima model[11], Yoon and Kim's model[12] and its extended form[13]. The limitation for these models is that it is necessary to determine the zeta potential or Debye-Hückel parameter. Accurate measuring of zeta potential needs a correction coefficient which is a function of Debye-Hückel paprameter. For a suspension with added electrolyte, the Debye-Hückel parameter can be explicitly calculated from ionic strength which can be calculated from the concentration of added electrolyte. But for a deionized suspension where the free counterions mainly come from the dissociation of charged particle, the estimation of Debye-Hückel parameter cannot be easily solved especially when counterion condensation or dissociation equilibrium needs to be considered.

From the above models for measuring effective charge, Hessinger's model isn't involved with the calculating of the Debye-Hückel parameters nor determining μ^{∞}. Once the effective charge is determined, the Debye-Hückel parameters can be calculated as well as zeta potential. Hessinger's model is the approach taken here. Experimentally, the particle sizes of CUPs were determined by dynamic light scattering. The conductivity and electrophoretic mobility at different concentrations were measured by Malvern Nano ZS zetasizer.

1.3 EXPERIMENTAL AND MATERIALS

1.3.1 Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. Methyl ethyl ketone, acetone and tetrahydrofuran were purified by distillation. Monomers were purified to remove contaminants and inhibitors. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Deionized water was used for all experiments.

1.3.2 Synthesis and Characterization of Poly(MMA/MAA) Copolymers. Copolymers of MMA and MAA were prepared in a molar ratio of 9:1 by free radical polymerization in methyl ethyl ketone (MEK) and refluxed for 24 hours under argon. AIBN (0.073 mole % to monomers) as the initiator and 1-dodecanthiol as chain transfer agent were used. The un-reacted monomers and solvent were removed in-vacuo. The product was dissolved in distilled acetone and precipitated in de-ionized water. The polymer was dried at 50°C in a vacuum oven. The absolute molecular weight of the copolymers was measured using gel permeation chromatography by Viscotek model 305 manufactured by Malvern Corp. Flow rate of THF was 0.5ml/min, and the injection volume 100μl. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight.

1.3.3 Acid Number. Acid numbers (AN) were measured by the titration method found in ASTM D 974; modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, and phenolphthalein in place of methyl orange. The titration was performed in tetrahydrofuran as solvent.

1.3.4 Water-reduction. Polymers were dissolved in tetrahydrofuran (THF) (10% w/w) and stirred overnight. Sodium hydroxide was added to neutralize all the acid groups according to its acid number. To the solution was added an equal amount of water (pH=8.5~9 adjusted by NaOH) to THF by a peristaltic pump at a rate of 1.24g/minute, and the pH of solution was maintained between 8.5 and 9. THF was then stripped in-vacuo. Solutions were then filtered through 0.45μm Millipore membrane to remove any foreign materials which were typically measured to be less than 0.05% by weight. The solution was diluted to different concentrations with pH modified water (pH was between 8.5 and 9). Higher concentrations were attained by stripping the water in-vacuo.

1.3.5 Density of Dry CUPs. The suspensions of CUP were dried in vacuum oven heated at 50℃ in presence of solid sodium hydroxide to absorb carbon dioxide. The sample was then heated at 110℃ to constant weight. The density of the dry cup was measured by a gas displacement pycnometer: Micromeritics AccuPycII 1340. Volume of sample can be calculated as:

$$V_s = V_c + V_r/(1 - \frac{P_1}{P_2}) \tag{8}$$

where V_s is the sample volume, V_c is the volume of the empty sample chamber, V_r is the volume of the reference volume, P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. Equilibrium flow rate of Helium gas is 0.005psig/min, temperature was controlled at 25.89±0.04℃. Twenty five readings were made for each sample, and the results were reported by its average and standard deviation.

1.3.6 Electrophorectic Mobility, Zeta Potential and Conductivity of CUPs. Electrophoretic mobility, zeta potential and conductivity of CUPs were measured by Zetasizer ZS 90S manufactured by Malvern, Inc. The samples with various volume fractions were prepared by dilution from a concentrated sample by water with the same pH of the original sample. For each sample, at least five measurements were run. For each run, at least 20 scans were made. The results were reported as the average with estimate of standard deviation. The instrument first measured the electrophoretic mobility of particle suspended in the solvent by Laser Doppler Velocimetry. The detecting system is Mixed Mode Measurement-Phase Analysis Light Scattering (M3-PALS)[14] so that electroosmosis effect was avoided and the true electrophoretic velocities were obtained.

1.4 PRELIMINARY EXPERIMENTAL RESULTS

1.4.1 Characterization of Polymers. The molecular weight, acid number and densities of the copolymer are listed on Table 1.1. The measured particle sizes of CUP were all in good agreement with the theoretical particle sizes which is calculated equivalent diameter of the sphere folded from a polymer chain with molecular weight Mn.

Table 1.1. Molecular weight, acid number , densities , theoretical and measured particle sizes of copolymers.

Mn^a	Mw^b	AN^c	$\rho_p{}^d$	$d_c{}^e$	$d_m{}^f$
36	45	57.7	1.2326±0.0015	4.5	4.6

a) Number average molecular weight, kg/mol; b) weight average molecular weight, kg/mol; c) Acid number, mgKOH/g; d) density of dry CUP, g/ml; e) theoretical particle size Mn by $d_c = \sqrt[3]{\frac{6M_n}{\pi\rho_p N_A}}$, nm f) measured particle size by dynamic light scattering, nm.

1.4.2 Electrophoretic Mobilities, Conductivities and Effective Charges. The electrophoretic mobility of CUPs and the conductivity of the suspensions at different number densities were presented in Figure 1.1.

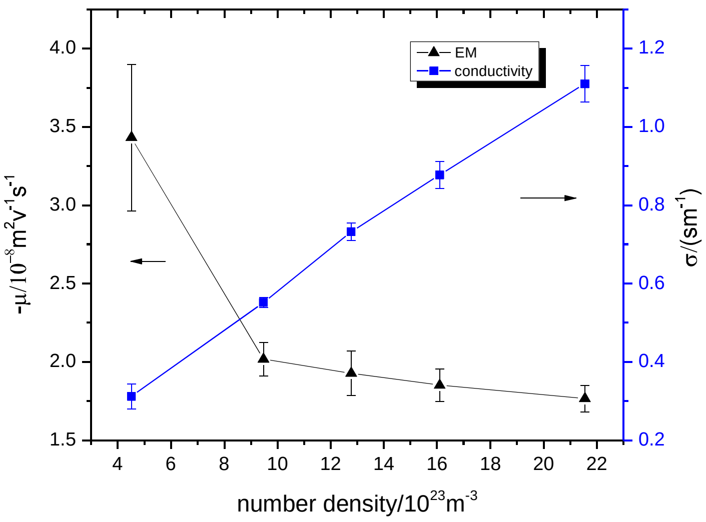


Figure 1.1. Electrophoretic mobilities and conductivities of CUPs suspension at various number densities.

Figure 1.1 shows that the conductivity of CUP increased with number density close to linearly indicating that there is no significant additional counterion condensation in the studied concentration range. The effective charges at each concentration were calculated by Equation 7. The results were presented in Figure 1.2 along with the predicted values from Belloni's program. The agreement was majorly good except for the suspension with number density larger than 35×10^{23} /m^3. Based on the calculated results from Belloni's program, it is found that the effective charge values were sensitive on pH values and total ion concentration in the suspension. Although the pH values were controlled in the range of 9.5-9.6, minor fluctuations of pH caused fluctuation of effective charge.

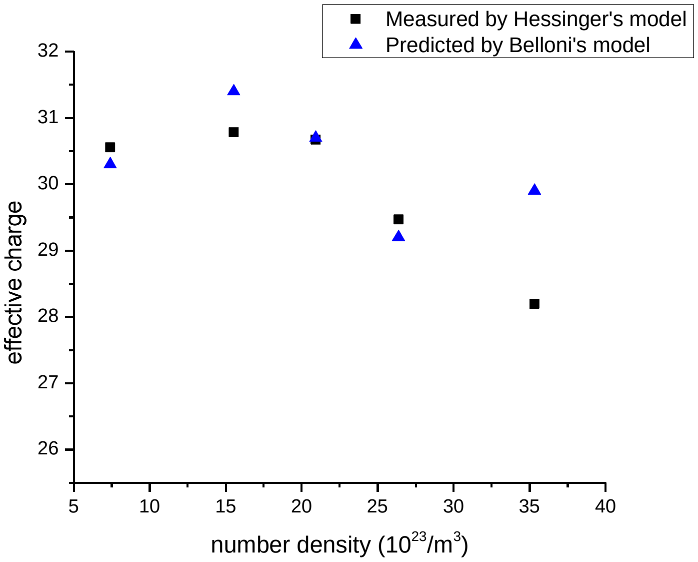


Figure 1.2. Effective charge calculated from Hessinger's model and from Belloni's prediction.

The behavior of electrophoretic mobility of the CUP in this study is similar to the simulation result of charge particle[15] with radius of 4 nm and effective charge of 60, and was also similar to the experimental results of monodisperse latex[15]. The general reason was that the electrophoretic mobility decrease with increasing values of κR_s when κR_s is between 0.1 and 10^{16}. If the values of κ were calculated with Equation 9 where Z_{eff} is the effective charge numbers calculated from Equation 7, the values of κR_s were found to fall between 1.1 and 2.3. Therefore, the experimental values qualitatively agreed with the trend predicted in theory[16].

$$\kappa^2 = \frac{e^2}{\varepsilon_0 \varepsilon_r k_B T}(nZ_{eff} + 2000N_A \cdot 10^{pH-14}) \qquad (9)$$

In salt-free suspension, the value of κ was proportional to the square root of number density of CUPs as shown in Equation 8 due to the contribution of the counterion dissociated from the charged particle when there was no significant counterion condensation, i.e., Z_{eff} does not change significantly. Thus, as the concentration of charge particles increases, κ increases, so does κR_s.

Due to technical limitation, the electrophoretic mobility at very low or very high number density cannot be measured. Since the particle is very small, when the solution is very dilute, the signal to noise from the scattering is very low. If the suspension is very concentrated, the suspension in the capillary cell can easily get heated and form bubbles in the cell. For concentrated suspension, fast signal gathering is required so that the sample will not be significantly heated during measuring. For diluted suspensions, it is desired to have a higher sensitive detecting system so that the electrophoretic mobility of CUPs at low concentration can be evaluated, and the theoretical prediction[16] in dilute regime can be further justified.

1.5 CONCLUSION

In summary, the electrophoretic mobilities and conductivities of CUP as a function of concentration have been investigated. When the number density of the CUP particle is between 4×10^{23} and 2.1×10^{24}/m^3, there was no significant counter ion condensation. The electrophoretic mobilities were found to decrease with increasing number densities as classical prediction. More research work needs to be done for different molecular weights in both salt-free and salt-added suspensions. In order to evaluate the electrophoretic mobilities of CUPs suspension in low concentrations, detecting system with higher sensitivity is required.

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PAPER

I. RHEOLOGICAL STUDIES ON COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES SUSPENSIONS

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ABSTRACT

A study about rheological behavior of Colloidal Unimolecular Polymer (CUP) particles in water was evaluated. The intrinsic viscosities were determined for CUP with different molecular weights and specific viscosities were fit with a model considering hydrodynamic interaction and electroviscous effects. It was found that the CUP surface had a layer of water which increases with particle size or molecular weight. The effective charges on the surface of particle were calculated and correlate with the rheological behavior of CUP from dilute to semi-dilute range. The predicted values were in good agreement with the experimental up to volume fraction of 0.08.

Keywords: Colloidal Unimolecular polymer, electroviscous effect, surface water

1. INTRODUCTION

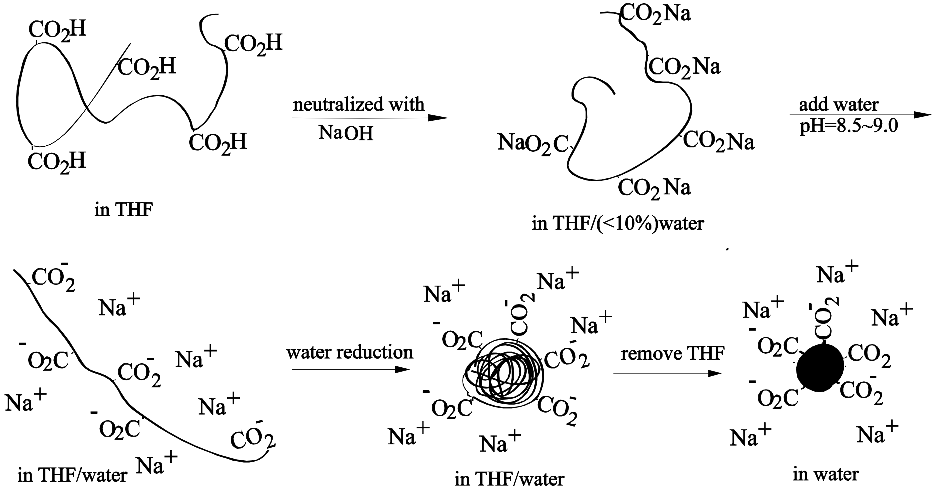
In past decades, many researchers have devoted their efforts to study the physical and chemical properties of polyelectrolytes since knowledge about polyelectrolytes will shed light on the fundamental properties of bio-macromolecules like proteins and virus. Similar to a variety of bio-macromolecules in terms of conformation, polyelectrolytes also exists in various forms such as rod-like, random coil, and spherical. Spherical polyelectrolytes attract special attention since most proteins fold into globular domains. There were several major types of spherical polyelectrolytes: spherical polyeletrolyte brush with hydrophobic core and hydrophilic brushes[1, 2], surface modified latex[3], and surface modified fullerene[4].

Colloidal Unimolecular Polymer (CUP) particles are a new type of true nanoscale material.[5] CUPs are formed by the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent. The formation of CUP particles is driven by the polymer-polymer interaction being greater than the polymer-solvent interaction and entropically favored by release of the water analogously to micelle formation with hydrophilic or charged groups creating the sphere-like shape. Scheme 1 shows the formation of CUP particles with carboxylate groups on the surface, keeping the particles from aggregation. Once formed these colloidal particles are thermodynamically stable.[6]

The CUP suspension contains only charged particles, water and counterions. Compared with the spherical polyeletrolyte mentioned above, there are several advantages of CUPs being treated as model material to study protein. First, CUP is formed by a single strand of polymer chain while spherical polyeletrolyte brush is formed by a core attached with a lot of linear polyelectrolyte chains. Thus, the conformation of CUP is closer to globular protein's. Second, CUPs is free of surfactant and the preparation procedure is quite simple while surface modified latex involves with tedious dialysis to remove the surfactant. Third, the size and charge density can be easily modified while the size of surface modified fullerene is not easy controlled. Therefore, CUP is a very good model material to study the fundamental properties of protein or analogous particles.

In addition, as an innovative material, CUP can find its application area in coating, drug delivery, catalyst matrix, etc. Therefore, it is important to investigate the basic properties of CUP particles. Among the basic properties of polyelectrolytes, rheology is of great importance since they related with conformation, diffusion, structure, even their surface behavior. This work presented a primary study on rheology behavior of CUP aiming at providing a foundation for further studying the colloidal properties of CUP.

Scheme 1. Process of forming CUP particles from poly(methyl methacrylate-co-methacrylic acid).



Scheme 1 illustrates the formation of CUP particle and the surface charges keep the CUPs stable in the suspension. Researchers have studied the rheology behavior of many charge stabilized colloid particles such as latex[7] and silica[8]. The charged groups are hydrophilic and will adsorb a layer of water molecules to the surface of the particle. The structure of surface water is dependent on many factors such as roughness, surface chemistry, charge density etc. From the intrinsic viscosity of the suspension, the extent of hydration of the CUPs can be estimated similar to the case of protein[9]. Correlated with the density and molecular weight of CUPs, the thickness of water layer on each particle can also be estimated.

Compared with regular latex and silica, there are several advantages of CUP as a material to study rheological behavior. First, unlike latex particles, CUP does not contain surfactants or emulsifiers that will have some effect on the viscosity of the suspension. Secondly, the size of CUP particles can be manipulated in a range from 2 to 9 nanometers[6]. These small sizes make them an excellent material to study the effect that the surface water has on the solid content and rheology behavior. Besides, CUPs are easily and inexpensively made compared with some other materials like nano colloidal gold. Brader[10] has made an excellent review on research works which described the rheology behavior of hard spheres in water, but none of them have considered the effect of surface water or bound water on the rheology behavior of viscosity. This effect can be neglected when the size of particle is very large. For instance, the size of a typical latex particle is about 100nm and the diameter of a water molecule is only 0.28nm. Assume that there is one layer of water bound on the surface of a particle, the ratio of volume of bound water to latex particle is only 0.0084:1. However, when the particle is as small as 3 to 9 nm, the ratio can increase up to 0.67:1, which significantly increases the effective volume fraction as surface water. Without considering other effects like the electroviscous effect, it can be expected that the rheology behavior of CUP particles will be more complicated than a regular colloid in view of Einstein's viscosity theory of hard spheres relating the viscosity of a colloid suspension with the volume fraction of a solid particle. In the present work, electroviscous effect, hydrodynamic perturbation, and surface water will be evaluated in the case of the rheological behavior of CUP particles.

2. THEORETICAL BASIS

2.1 Calculation of Effective Charge on the Surface of CUPs. The CUPs in this study resulted from the copolymerization of methyl methacrylate and methyl methacrylic acid. The surface charged groups originated from neutralization of carboxylic acid, which is a weak acid. In solution with pH range 8.5-9, the effective charge on surface will be subject to the dissociation equilibrium. In addition, there exists short-range and long-range counterion condensation[11]. The former one is due to the repulsion energy between the adjacent charged groups on the same particle; the latter one is due to repulsion energy between the charged groups on the adjacent particles when the concentration is high. Ninham and Parsegian[12] first proposed a model in which the surface of a colloid contains ionizable groups which dissociates depend on the counterion atmosphere. The basic idea is that two electro repulsive surfaces tend to minimize the total free energy. Based on that theory, Belloni[13] further developed a simple program to calculate the effective charge as long as the particle size, maximum bare charge, pKa of the ionizable groups, pH of the reservoir solution, and salinity of the reservoir are known. Other than the model mention above, there are also some other models to determine effective charge such as O'Brien-White-Oshima model[14, 15], Yoon and Kim's model[16] and its extended form[17]. The limitation for these models involves determining the zeta potential or Debye-Hückel paprameter. Accurate measurement of the zeta potential needs a correction coefficient which is a function of Debye-Hückel paprameter. For a suspension with added electrolyte, the Debye-Hückel parameter can be explicitly calculated from ionic strength which can be calculated from the concentration of added electrolyte. But for a deionized suspension where the free counterions mainly come from the dissociation of the charged particle, the estimation of Debye-Hückel parameter cannot be easily solved especially when counterion condensation or dissociation equilibrium need to be considered. In this study, the effective charges are calculated by Belloni's program by entering necessary parameters such as particle sizes at each volume fraction.

2.2 Determination of Intrinsic Viscosity of CUPs. While it is quite a well-developed method to determine the intrinsic viscosity of uncharged polymer by extrapolating the reduced viscosity to infinite dilution, there is no common method to determine the intrinsic viscosity of polyelectrolyte solution without added electrolyte. In many cases, the reduced viscosity of polyelectrolytes does not approach a set value when the concentration is dilute. It may increase sharply and sometimes a maximum value was observed. Many methods have been attempted to determine the value of intrinsic viscosity. One of them is derived from the relation of relative viscosity,ηrel with volume, ϕ, by eq. 1 at dilute concentration[18] where $[\boldsymbol{\eta}]_{\phi}$ is intrinsic viscosity in term of volume fraction.

$$\ln(\eta_{rel}) = [\eta]_{\phi}\phi \tag{1}$$

In this study, this method will be used to determine the intrinsic viscosity of CUP suspension.

2.3 Rheological Models for CUPs with Electroviscous Effect. Electroviscous effects are normally categorized by three types: primary, secondary and tertiary. The distortion of the electrical double layer around the charged particle cause additional energy dissipation under shear. This effect is called the primary electroviscous effect (1EE). When particles approach each other, the electrical repulsion between electrical double layers increases the viscosity of suspension. This effect is so-called the secondary electroviscous effect (2EE). The tertiary electroviscous effect (3EE) is referring to the expansion or contraction of particles due to change of conformation especially to polyelectrolytes[19, 20]. In this section, a brief introduction about electroviscous effects will be given to present the models and theories which will be used in this study. For 1EE, Smoluchowski[21] first raised the concept of a primary electroviscous coefficient, *p*, and presented the intrinsic viscosity as eq. 2 where $\boldsymbol{\varepsilon_r}$ is the dielectric constant of the solvent, $\boldsymbol{\varepsilon_0}$ is the permittivity of a vacuum, *k* is the specific conductivity of the continuous phase, $\boldsymbol{\zeta}$ is the zeta potential, and R_s is the radius of the spheres.

$$[\eta] = 2.5(1 + p) = 2.5[1 + 4(\varepsilon_r\varepsilon_0\zeta)^2/k\eta_0 R_s^2\ ] \qquad (2)$$

Other researchers reported a corrected primary electroviscous effect[22, 23]. The major changes were replacing specific conductivity of the continuous phase with the Debye length κ^{-1} which related 1EE with the electrical double layer. The Debye length κ^{-1} is calculated by eq. 3, where k_B is the Boltzmann constant, T is the temperature, N_A is Avogadro's constant, Z_i is the valence of the ions, M_i is the concentration of the various ions with unit mol/L.

$$\kappa^{-1} = 1/[\left(\frac{1000e^2 N_A}{\varepsilon_0 \varepsilon_r k_B T}\right) \sum_i Z_i^2 M_i]^{1/2} \tag{3}$$

Russel[24] further corrected the intrinsic viscosity of charged particle at the condition of large distortions of the electrical double layer when the shear rate is relatively high by eq. 4 where P_e is the Péclet number defined as $\mathrm{P_e} = \frac{\mathrm{R_S^2}}{\mathrm{D}} \dot{\gamma}$ where $\dot{\gamma}$ is the shear rate, D is the diffusion coefficient expressed as $\mathrm{D} = \frac{\mathrm{k_B T}}{6\pi\eta_0 \mathrm{R_S}}$.

$$[\eta] = 2.5[1 + \frac{6(\varepsilon_r \varepsilon_0 \zeta)^2}{k\eta_0 \mathrm{R_S^2}} \frac{1}{1+P_e^2}] \tag{4}$$

Equation 4 implies that a suspension of charged particles will undergo shear thinning behavior. The most recently analytical expression of primary electroviscous coefficient, *p*, was derived by Watterson and White[23] and is presented as eq. 5

$$p \approx \frac{6\varepsilon_0 \varepsilon_r k_B T}{5\eta_0 e^2} \frac{\sum_{i=1}^{N} n_i^\infty Z_i^2 \lambda_i}{\sum_{i=1}^{N} n_i^\infty Z_i^2} L(\kappa R_s) (\frac{e\zeta}{k_B T})^2 \tag{5}$$

where η_0 is the viscosity of water, Z_i is the valence of the ions, λ_i is the drag coefficient of various ions in the solution, expressed as eq. 6 with Λ_i^0 as limiting equivalent conductance of each ion. $L(\kappa R_s)$ is a function of κR_s, expressed as eq. 7

$$\lambda_i = \frac{N_A e^2}{\Lambda_i^0} \tag{6}$$

$$L(\kappa R_s) = \frac{10\pi}{3} Z(\kappa R_s)(1 + \kappa R_s)^2 \tag{7}$$

where [22]

$Z(\kappa R_s) \approx (200\pi\kappa R_s)^{-1} + (\frac{11\kappa R_s}{3200\pi})$ for thick double layers, i.e., small κR_s, or

$$Z(\kappa R_s) = (\frac{3}{2\pi})(\kappa R_s)^{-4} \text{ for thin double layers, i.e., large } \kappa R_s. \tag{8}$$

As shown in Eq. 5, to calculate p involves the zeta potential which, as stated before, is not easily determined for CUP suspension without added electrolyte. One possible method to circumvent it is to relate the effective charge of particle with zeta potential by eq. 9[25]

$$\zeta = \frac{Q_{eff}}{4\pi\varepsilon_0\varepsilon_r R_s(1+\kappa R_s)} \tag{9}$$

In this study, eq. 5 was used to estimate the primary electroviscous coefficient. As the concentration of suspension increases from dilute to semi-dilute range, the 2EE started to play a role when the electrical double layer senses the presence of near particles. Russel[26] developed a rheological model as eq. 10 for charge stabilized suspensions which was second order in volume fraction when κR_s is small and interparticle distance is large.

$$\eta_{rel} = 1 + [\eta]\phi + \frac{2}{5}([\eta]\phi)^2 + \frac{3}{40}\ln\left(\frac{\alpha}{\ln(\alpha)}\right)(\kappa L)^4 \frac{\phi^2}{(\kappa R_s)^5} + O(\phi^3) \tag{10}$$

In eq. 10, $[\eta]$ is the intrinsic viscosity including 1EE, α represent the ratio of electro repulsion force to Brownian motion, defined as eq. 11 where ψ_s is the surface potential of the charged particle, A is a complicate function of κR_s and interparticle distance and varies from 0.6 to 1, increasing with interparticle distance[27]

$$\alpha = A(4\pi\varepsilon_0\varepsilon_r\psi_s^2 R_s^2\kappa)\exp(2\kappa R_s)/k_BT \tag{11}$$

and L is the effective collision diameter defined as eq. 12.

$$L = \kappa^{-1} \ln[\frac{\alpha}{\ln\left(\frac{\alpha}{\ln(\alpha)}\right)}] \tag{12}$$

In eq. 10, the surface potential is also not easily determined for CUP suspensions without salt. The reason is similar to the zeta potential measurement. Likely, an analytical expression derived by Ohshima[28] can be used to estimate the value when the surface potential is high, eq. 13.

$$\psi_s = \frac{k_B T}{ze} \ln[\frac{1}{6\phi \ln\left(\frac{1}{\phi}\right)} (\frac{ze}{k_B T})^2 (\frac{Q_{eff}}{4\pi\varepsilon_0\varepsilon_r R_s})^2] \tag{13}$$

$$\text{if} \quad \frac{Q}{4\pi\varepsilon_0\varepsilon_r R_s} \cdot \frac{ze}{k_B T} > \ln(\frac{1}{\phi})$$

As for tertiary electroviscous effect, there is no much research work in this areas. In this study, the material is a rigid solid sphere at room temperature. The only possible conformation change would be the volume fraction occupied by the surface water layer. Supposed that the thickness of water layer is δ, the effective volume fraction will be expressed as eq. 14

$$\phi_{eff} = \phi(1 + \frac{\delta}{R_s})^3 \tag{14}$$

In this study, the intrinsic viscosities for each CUP with different molecular weight will be determined from the slope of ln η_{rel} versus volume fraction. Combined with the densities of the CUPs, the water layer thickness for each particle will be estimated. The effective charge of CUPs at various volume fractions will be calculated by Belloni’s program. Based on that, the Debye-Hückel parameter, zeta potential, primary electroviscous coefficient, and effective collision diameter will be calculated. The experimental viscosity will be compared with the prediction made by eq. 10.

3. EXPERIMENTAL SECTION

3.1 Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. Methyl ethyl ketone, acetone and tetrahydrofuran were purified by distillation. Monomers were purified to remove contaminants and inhibitors. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Deionized water was used for all experiments.

3.2 Synthesis and Characterization of Poly(MMA/MAA) Copolymers. Copolymers of MMA and MAA were prepared in a molar ratio of 9:1 by free radical polymerization in methyl ethyl ketone (MEK) and refluxed for 24 hours under argon. AIBN (0.073 mole % to monomers) as the initiator and 1-dodecanthiol as chain transfer agent were used. The un-reacted monomers and solvent were removed in-vacuo. The product was dissolved in distilled acetone and precipitated in de-ionized water. The polymer was dried at 50°C in a vacuum oven. The absolute molecular weight of the copolymers was measured using gel permeation chromatography by Viscotek model 305 manufactured by Malvern Corp. Flow rate of THF was 0.5ml/min, and the injection volume 100μl. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight.

3.3 Acid Number. Acid numbers (AN) were measured by the titration method found in ASTM D 974; modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, and phenolphthalein in place of methyl orange. The titration was performed in tetrahydrofuran as solvent.

3.4 Water-reduction. Polymers were dissolved in tetrahydrofuran (THF) (10% w/w) and stirred overnight. Sodium hydroxide was added to neutralize all the acid groups according to its acid number. To the solution was added an equal amount of water (pH=8.5~9 adjusted by NaOH) to THF by a peristaltic pump at a rate of 1.24g/minute, and the pH of solution was maintained between 8.5 and 9. THF was then stripped in-vacuo. Solutions were then filtered through 0.45μm Millipore membrane to remove any foreign materials which were typically measured to be less than 0.05% by weight. The solution was diluted to different concentrations with pH modified water (pH was between 8.5 and 9). Higher concentrations were attained by stripping the water in-vacuo.

3.5 Density of Dry CUP. The suspensions of CUP were dried in vacuum oven heated at 50℃ in presence of solid sodium hydroxide to absorb carbon dioxide. The sample, clear crystal-like material was then heated at 110℃ to constant weight. The density of the dry cup was measured by a gas displacement pycnometer: Micromeritics AccuPycII 1340. Volume of sample can be calculated as:

$$V_s = V_c + V_r/(1 - \frac{P_1}{P_2}) \tag{15}$$

where V_s is the sample volume, V_c is the volume of the empty sample chamber, V_r is the volume of the reference volume, P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. Equilibrium flow rate of Helium gas is 0.005psig/min, temperature was controlled at 25.89±0.04℃. Twenty five readings were made for each sample, and the results were reported by its average and standard deviation.

3.6 Shearing Viscosities of CUP Solutions. One milliliter of CUP solution was transferred to the well of the Brookfield LV DVIII by Eppendorf pipet. The well's temperature was controlled at 25.0±0.1℃ by a circulating constant temperature water bath. Shearing viscosities of CUP under a series of shear rate were measured. The shear rates were programmed to increase at set speed and viscosities were recorded after continuously shearing for 1 minute at each speed.

3.7 Absolute Viscosity of CUP Solutions. The CUP suspension was transferred to an Ubbelohde capillary viscometer, which was in a constant temperature water bath at 25.0±0.1℃. The suspensions were equilibrated for 20 minutes with plastic wrap covered on top of viscometer to prevent evaporation and CO_2 contamination. A stop watch with 0.01 second precision was used to monitor the elution time. The estimated standard error was within 0.5%. Absolute viscosity was calculated by eq. 16

$$\eta = t \cdot d \cdot c \tag{16}$$

where t, d, and c were elution time, density of solution and constants of Ubbelohde with units second, g/ml and cP/second respectively. The relative viscosity of solution was calculated as

$$\eta_r=\eta/\eta_w \tag{17}$$

where η_w is the viscosity of water with unit cP. Densities of solutions were measured with pycnometer at 25.0±0.1℃.

3.8 Particle Size of CUP and Distribution. Particle size and distribution were measured by dynamic light scattering, Microtrac Nanotrac 250. The viscosity of suspension was used instead of water. The reason will be presented below. The Ultrafine particle analysis mode was used.

4. RESULT AND DISCUSSION

4.1 Characterization of Polymers. The molecular weight, acid number and densities of the copolymers are listed on Table 1. It shows that the composition of the copolymers had similar acid numbers. The densities of dry CUP increase with increasing molecular weights as expected since the weight fraction of end groups decreased with increasing molecular weight.[29]

Table 1. Molecular weight, acid number and densities of copolymers.

sample ID	Mn (g/mol)	Mw (g/mol)	acid number (mgKOH/g),AN	Density of dry CUP (g/ml), ρ_p
polymer 1	28,000	35,000	59.1	1.2246±0.0018
polymer 2	36,000	45,000	57.7	1.2326±0.0015
polymer 3	111,000	174,000	62.0	1.2342±0.0018

4.2 Particle Size Analysis. The particle size of CUP was measured by Microtrac Nanotrac 250 with dynamic light scattering. The instrument first measured the diffusion coefficient of particle in the media, then calculated the particle size by Stokes-Einstein equation as shown in eq.18

$$\mathrm{D} = \frac{k_B T}{6\pi\eta r} \tag{18}$$

where $\mathrm{k_B}$ is the Boltzman Constant, T is the absolute temperature of solution, η is the viscosity of solvent and r is the radius of particle. Since the CUP is a nanoscale charged particle, the method needed some justification for following reasons. First, the particle size was about 3-9 nm, very small compared with working wavelength of laser signal (780nm), therefore the signal of scattering light from the surface of particles was relatively low. In order to increase the signal of the scattered light, the volume fraction needed to be increased up to around 10% instead of infinite dilution. Since the particle was very small, there will be no issue of multiple scattering. However, high concentration can cause another issue: the charged particles will have strong electronic repulsion that makes the eq. 18 no longer valid. One of the frequently used methods has been to correct eq. 18 with reduced osmotic pressure $(\frac{\partial \pi}{\partial c})_T$. Since measuring the osmotic pressure of colloid dispersion is often very time-consuming, it is not a convenient way. Therefore, another method was employed.

The relationship between viscosity and diffusion coefficient have been extensively studied from the classical Stokes-Einstein model which is valid for dilute systems like those described in eq. 18. When the suspension system is at higher concentration, the relationship is more complicated. A generalized Stokes-Einstein relation (GSE) has been derived from many researches[30]. At various volume fractions ϕ, the relationship between zero-limiting shear viscosity of the suspension $\eta(\phi)$ and the long-time self-diffusion coefficient $D_L^S(\phi)$ can be represented by eq. 19 or 20 which have agreed well with experiments in solid Polystyrene[31], micelles[32], and silica[33].

$$\frac{\eta(\phi)}{\eta_0} = \frac{D_0}{D_L^S(\phi)} \tag{19}$$

or $$D_L^S(\phi) = \frac{kT}{6\pi\eta(\phi)r} \tag{20}$$

In the case of charge stabilized silica[34], the approximation was good in the dilute range when the volume fraction was less than 0.1. For higher volume fraction, the hydrodynamic interaction between charged particles is far larger than Brownian motion from solvent molecules, thus the GSE is no longer valid. When the Microtrac Nanotrac 250 was used to measure the particle size of CUPs, according to the instruction of the manufacture, the viscosity of solvent was entered as an important parameter to calculate the particle size. However, the volume fraction of CUP was approximately 0.08 for sufficient scattered light intensity, far away from infinite dilution, so the diffusion coefficient was no longer D_0, or self-diffusion coefficent, but $D_L^S(\phi)$, the collective diffusion coefficient. Therefore, according to eq. 20, the viscosity of solution needs to be entered in order to calculate particle size.

Practically, first the loading index of CUP solution in Nanotrac 250 was measured to make sure the concentration was high enough to get valid light scattering signal intensity. Then the shearing viscosities of the sample solution were measured by Brookfield DV-III. Then the shear stress and shear rates were fitted by Casson's model[35] as illustrated by eq. 21 where τ is the shear stress, τ_0 is the yield stress, η is the plastic viscosity, D is the shear rate.

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta D} \tag{21}$$

If τ_0 was zero, it represents a Newtonian fluid. If not, it was a non-Newtonian fluid. If the CUP solution behaved as a Newtonian fluid, then the plastic viscosity was treated as its viscosity at the temperature. If not, the shear stress and shear rate were fitted with the power law model as eq. 22 where k is the consistency index with units of centi poise, and n is the flow index.

$$\tau = kD^n \tag{22}$$

If n>1, the fluid shows shear-thickening behavior; if n<1, it is shear-thinning. The more n deviates from 1, the more shear-thinning or shear-thickening will the fluid be. The viscosity used to enter into the DLS software will be the value of the consistency index, which was also the viscosity of the fluid at a shear rate of 1 Hz. Using the viscosity of the suspension, the particle sizes were measured. The results are listed in Table 2.

The results show that the measured number average diameters were similar to calculated diameter from number average molecular weight. The distributions from the GPC for the three polymers were compared with DLS in terms of fraction of passing. The molecular weights determined from GPC were converted to particle sizes based on assumption that each polymer chain collapse into a dense sphere and the density was same as the bulk. The fractions of passing were plotted along with the DLS data in Figures 1(a-c). The particle sizes determined from the molecular weight produced both average size and distribution which were in very good agreement with that of DLS. It indicated that most of the polymer chains have undergone single-chain self-assembling into an individual particle

Table 2. Particle size of CUP measured from Nanotrac 250.

sample ID	Mn[a] (kg/mol)	d_m[b]	d_c[c]
polymer 1	28	4.2	4.2
polymer 2	36	4.6	4.5
polymer 3	111	6.5	6.6

a) Average molecular weight by number b) Measured average diameter by number by DLS with unit nm c) calculated average diameter from Mn by $d_c = \sqrt[3]{\frac{6M_n}{\pi \rho_p N_A}}$ with unit nm

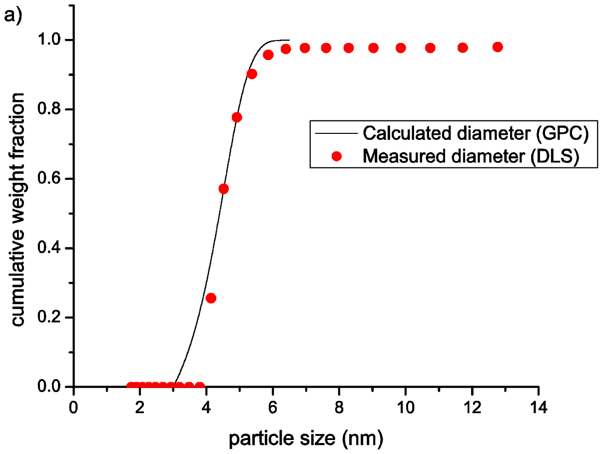


Figure 1. GPC and DLS for polymer 1,2,3. a) polymer 1;b) polymer 2;c) polymer 3.

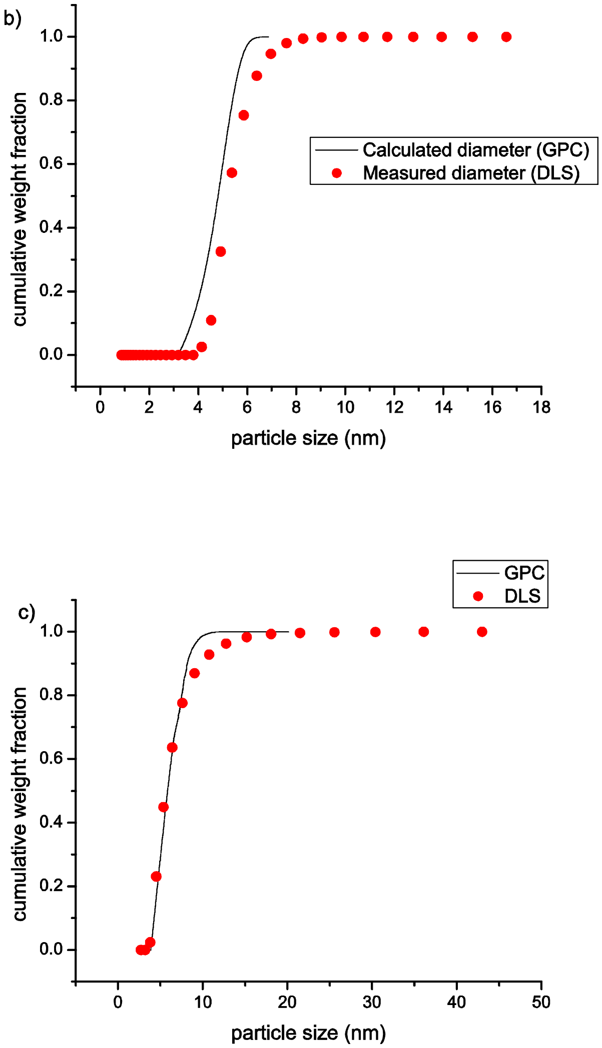


Figure 1. GPC and DLS for polymer 1,2,3. a) polymer 1;b) polymer 2;c) polymer 3. (Cont.)

4.3 Specifc Viscosity of CUP Suspensions. The specific viscosities of CUP suspensions were measured and plotted against volume fractions for the three polymers. Figure 2 shows that the specific viscosities of the three polymers at low volume fractions.

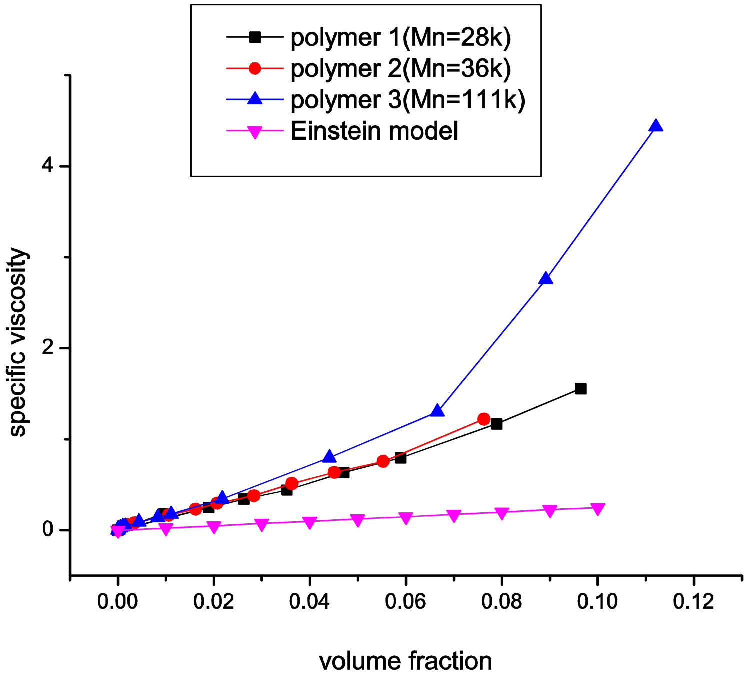


Figure 2. Specific viscosities of CUP suspensions for different molecular weight as function of volume fraction.

All of the samples unsurprisingly deviated from Einstein's model, even from the very dilute range. The ln η_{rel} were also plotted against volume fraction in Figure 3. Since it is reported that the intrinsic viscosity determined in this way is a function of volume fraction[36], the highest volume fraction were taken as 0.08 arbitrarily so that most of data of all polymers were in the same range. The intrinsic viscosities at low concentration were read from the slopes.

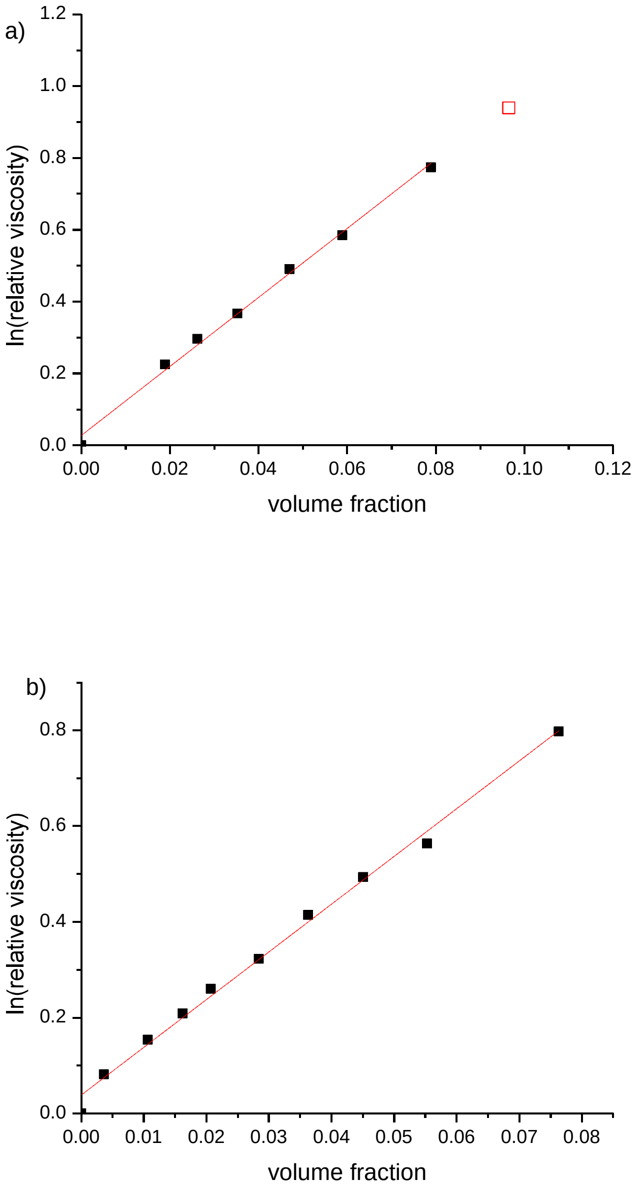


Figure 3. ln ηrel~ϕ for CUPS. a)CUP-1;b)CUP-2; c)CUP-3. Open points were masked points where the volume fraction is larger than 0.08.

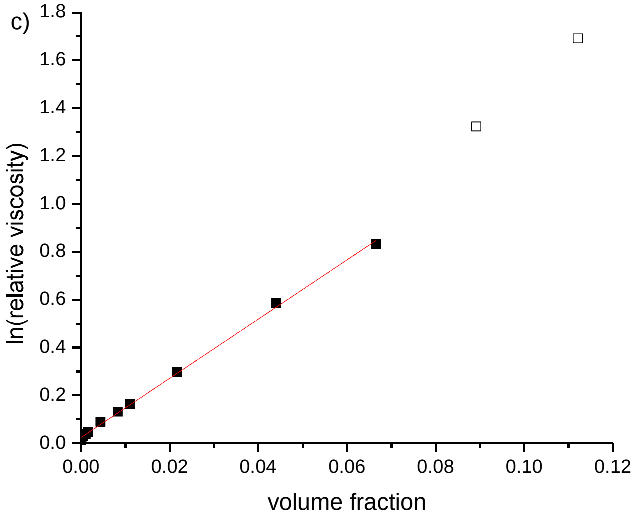


Figure 3. ln ηrel~ϕ for CUPS. a)CUP-1;b)CUP-2; c)CUP-3. Open points were masked points where the volume fraction is larger than 0.08. (Cont.)

Table 3. Intrinsic viscosities and calculated associated water of three CUPs reduced from the three polymers.

CUP	$[\eta]_\phi$	$\Delta[\eta]_\phi$ [c]	Adj. R^2	β[a]	δ[b]
1	9.61	0.28	0.995	2.3	0.88
2	9.97	0.26	0.994	2.4	1.02
3	12.37	0.17	0.998	3.2	1.9

a) associated water fraction in gram water per gram CUP ;b) thickness of water layer, nm; c) stand error of $[\eta]_\phi$

The associated water fraction, β, is defined as the ratio of surface water to CUP by weight. The value can be semi-quantitatively calculated by eq. 23[25] where $\frac{\rho_1}{\rho_2}$ is the density ratio of water to CUP (ρ_1 is 0.997 at 25℃).

$$\beta = \frac{\rho_1}{\rho_2}(\frac{[\eta]}{2.5} - 1) \tag{23}$$

Then if we further assume that each particle is spherical and surrounded by a uniform layer of water molecules with thickness δ, then δ can be expressed as eq. 24.

$$\delta = R_s[(\frac{\beta\rho_2}{\rho_1})^{\frac{1}{3}} - 1] \tag{24}$$

The results of β and δ are listed in Table 3. The data indicates that there are significant amounts of water on the surface of particles. The thickness of water layer increases with molecular weight. Although this trend needs more data to verify, it is reasonable that the thickness of water layer will increase along with the radius of particle. The difference among these polymers was only the molecular weight. If all acid groups were neutralized and dissociated, and the particle was spherical, then the bare surface charge density of CUPs without counterion condensation can be estimated by eq. 25

$$\sigma = (\frac{M_n}{4\pi})^{\frac{1}{3}} \cdot (\frac{3}{\rho N_A})^{-\frac{2}{3}} \cdot \frac{e}{m_{MMA}b + m_{MAA}} \tag{25}$$

where ρ is the density of polymer, N_A is Avogadro number, q is the elementary charge, m_{MMA} is the molecular weight of methyl methacrylate, m_{MAA} is the molecular weight of methacrylic acid, and b is the ratio of MMA to MAA by number in the copolymer which can be calculated from their acid numbers. The density of polymer and α was similar for the three polymers from Table 1, so surface charge density was roughly linear with the cube root of molecular weight of the polymer. The radius of particle can be expressed as $r = (\frac{3M_n}{4\pi\rho N_A})^{1/3}$, which means the radius of particle was also proportional to its molecular weight. In other words, the bare surface charge density was proportional to particle size.

The bigger the particle was, the stronger the surface charge density would be, or the more carboxylate groups are at the surface per unit area, which forms a thicker electrical double layer. Therefore, more counterions, i.e. sodium ions and associated water molecules, will be attracted to the surface. The larger charge densities of larger CUPs cause thicker surface water layers.

4.4 Fitting Specific Viscosities with Eq.10. In order to compare the experimental specific viscosities with the predicted values from eq. 10, the related parameters need to be calculated first. The surface potentials were calculated by eq. 13. The effective charge numbers, $\boldsymbol{Z_{eff}}$, were calculated by the Belloni's program. Then Debye-Hückel parameters were calculated by eq. 26 where pH is the pH values of solution. The summation of the

$$\kappa^2 = \frac{e^2}{\varepsilon_0 \varepsilon_r k_B T}\left(nZ_{eff} + 2000N_A \cdot 10^{pH-14}\right) \tag{26}$$

drag coefficents λ_i is dominated by sodium ion since the concentration of sodium dissociated from CUP is far larger than that of hydroxide, or hydronium. The zeta potentials, ζ, were calculated by eq. 9. With the calculated κ, ζ, λ_i, the primary electroviscous coefficient were calculated by eq. 5. The value of α, L were calculated by eq. 11 and 12. For α, its factor A ranges from 0.6 to 1, so there exist a minimum and maximum values of α. Some of these intermediate parameters were listed in Table 4. In right side of eq. 10, the first two terms can be treated as the contribution from primary electroviscous effect, tertiary electroviscous effect and hydrodynamic interaction. The high values of intrinsic viscosity were considered as the result of associated water. The second term contains ϕ^2 term which is normally related with hydrodynamic interaction. Thus the contribution from each effect can be calculated and plotted in Figure 4.

Table 4. Calculated intermediate parameters.

CUP	ϕ	$\eta_{sp}{}^{a}$	$Z_{eff}{}^{b}$	$\psi_s{}^{c}$	P	L(nm)
1	0.0189	0.252	9.2	0.079	0.016	11.1
	0.0262	0.345	8.7	0.070	0.013	9.7
	0.0352	0.444	8.3	0.062	0.011	8.6
	0.0470	0.633	7.8	0.054	0.009	7.6
	0.0589	0.795	7.4	0.047	0.008	6.9
	0.0789	1.168	6.9	0.039	0.006	5.9
	0.0964	1.559	6.6	0.034	0.006	5.3
2	0.0036	0.085	14.8	0.132	0.060	23.5
	0.0106	0.166	13.0	0.104	0.030	15.7
	0.0162	0.232	12.3	0.092	0.023	13.4
	0.0207	0.297	11.8	0.085	0.020	12.2
	0.0284	0.381	11.3	0.077	0.017	10.9
	0.0363	0.513	10.8	0.071	0.014	9.9
	0.0451	0.638	10.4	0.065	0.013	9.2
	0.0552	0.758	10.0	0.059	0.011	8.5
	0.0763	1.221	9.3	0.050	0.009	7.5
3	0.0001	0.024	36.0	0.231	0.623	133.1
	0.0005	0.029	33.1	0.199	0.305	83.6
	0.0011	0.039	31.5	0.180	0.199	63.1
	0.0016	0.048	30.6	0.169	0.156	53.8
	0.0044	0.095	28.4	0.144	0.088	36.8
	0.0083	0.141	27.0	0.128	0.062	29.0
	0.0111	0.177	26.4	0.121	0.053	26.1
	0.0217	0.348	24.8	0.105	0.038	20.6
	0.0441	0.797	22.9	0.088	0.028	16.3
	0.0665	1.300	21.7	0.078	0.024	14.3
	0.0892	2.758	20.7	0.071	0.021	13.1
	0.1121	4.432	19.9	0.066	0.019	12.3

a) Experimental measured specific viscosity; b) calculated effective charge by Belloni's program c) calculated surface potential, unit v

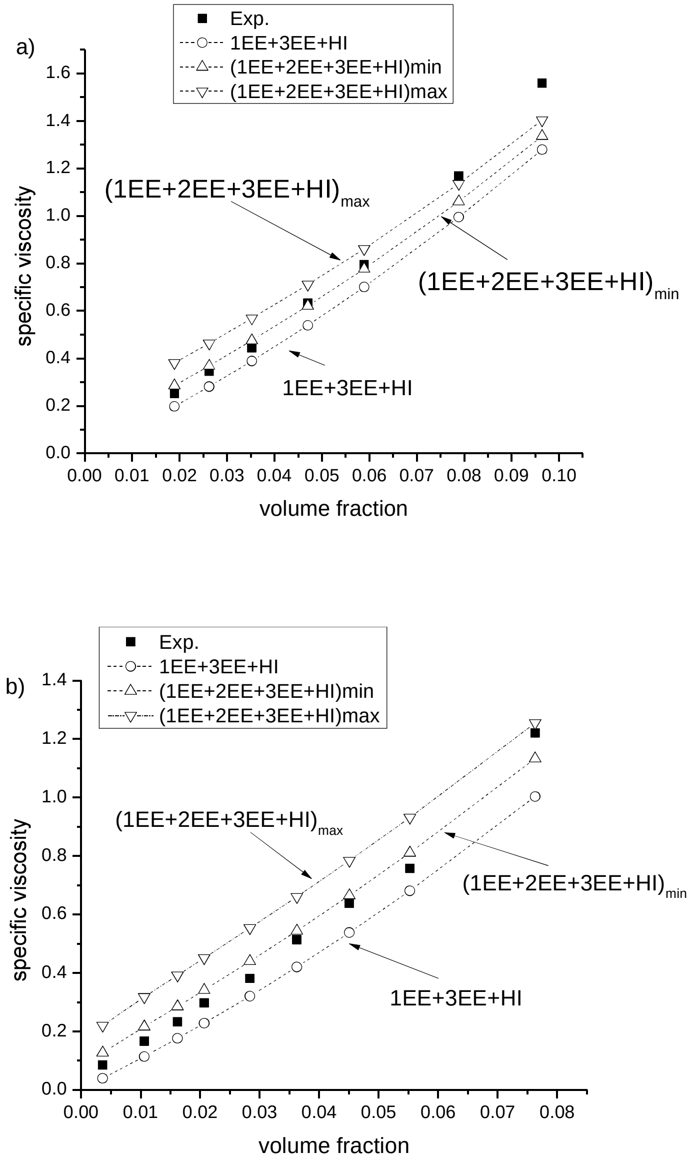


Figure 4. Comparison of experimental and predicted specific viscosities of CUPs. a) CUP-1; b) CUP-2; c) CUP-3.

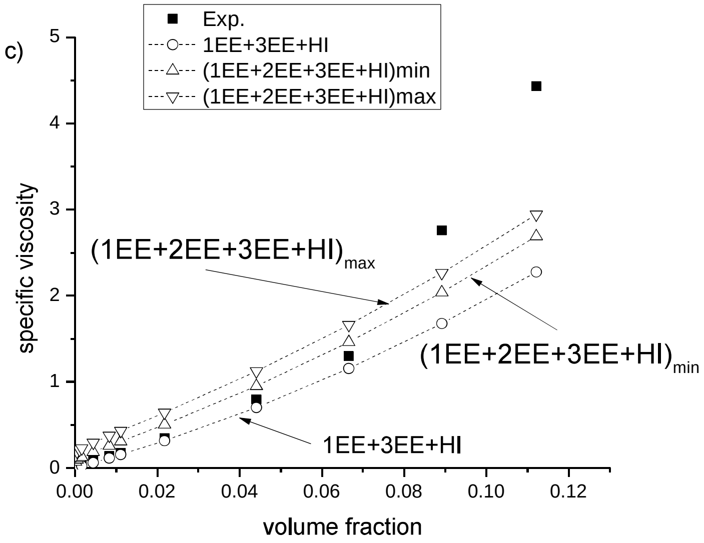


Figure 4. Comparison of experimental and predicted specific viscosities of CUPs. a) CUP-1; b) CUP-2; c) CUP-3. (Cont.)

As shown in Table 4, the primary electroviscous coefficients decrease sharply with increasing volume fraction. That was primarily due to the number of counterion increasing with volume fraction although the effective charge decreases with volume fraction. The increasing counterion shortens the electrical double layer and caused less distortion thus less energy dissipation. Since the *p* values drop sharply, the contribution of the primary electroviscous effect to total specific viscosity is not significant: the product of volume fraction with *p* is still low compared with the contribution of intrinsic viscosity. Similarly, the surface potentials drop with increasing volume fraction, countering the effect of surface potential to the repulsion energy. Thus effective collision diameters decrease with increasing volume fraction and the secondary electroviscous effect were not significant as shown in Figure 4. In all the three polymers, the theoretical values agree well with the experimental results when the volume fractions were lower than 0.08. In higher volume fraction range, except in CUP-2, the theory underestimated specific viscosities compared with experimental results. One possible correction would be the higher order of volume fraction to power three or even higher. Another one will be the correction of effective volume fraction by introducing the Crowding factor λ[37]. Then the effective volume fraction can be present as

$$\phi_{eff} = \frac{\phi}{1-\lambda\phi} \tag{27}$$

where λ ranges from 1.35 to 1.91 depending on maximum packing density. If λ is 1.35, when the volume fraction is 0.1, the difference between ϕ_{eff} and ϕ is 15%, which can bring the correction of more than 30% increase in viscosity due to the square term.

Figure 4 also indicated that tertiary electroviscous effect dominates the rheology behavior from dilute to semi-dilute range while the secondary electroviscous effect was not significant. In order to illustrate this, we can describe the rough picture of the structure of CUP by comparing the interparticle distance and effective diameters. With effective charge and number density, the Debye length, κ^{-1}, which is considered as thickness of electrical double layer can be calculated by eq. 26. Then the effective diameter of each particle d_{eff} can be expressed as

$$d_{eff} = 2(\kappa^{-1} + \mathrm{r}) \tag{28}$$

According to Wigner–Seitz cell model,[38] each CUP particle occupies a polyhedron space. The mean interparticle center-to-center distance d_{w-s} can be approximated to be eq. 29 where *n* is number density.

$$d_{w-s} = 2r_{w-s} \cong 2\left(\frac{3}{4\pi n}\right)^{1/3} \tag{29}$$

Thus the effective diameter and interparticle distances were calculated and presented in Figure 5.

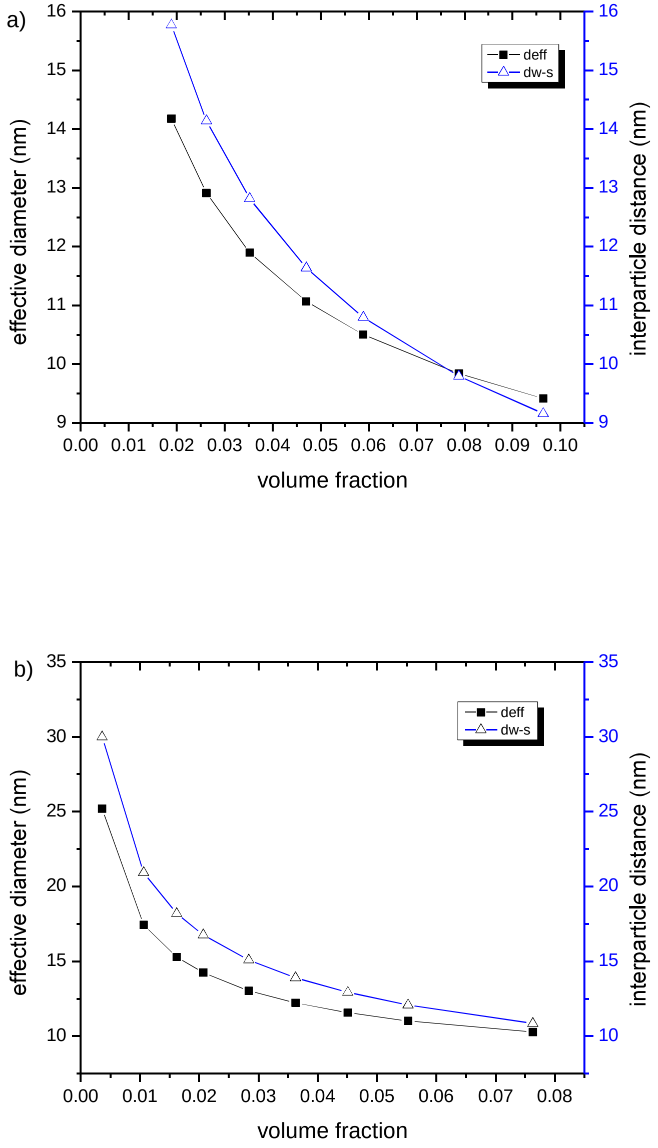


Figure 5. Comparison between effective diameter and mean interparticle distance. a) CUP-1;b) CUP-2; c) CUP-3.

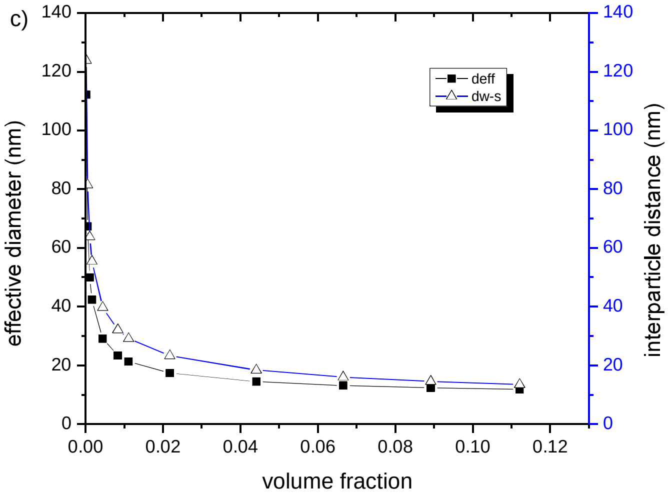


Figure 5. Comparison between effective diameter and mean interparticle distance. a) CUP-1;b) CUP-2; c) CUP-3.(Cont.)

As Figure 5 shows, the effective diameters gradually approached interparticle distance with increasing concentration. In CUP-1, when the volume fraction is near 0.08, the effective diameter is almost equal to interparticle distance: that seems to coincide with the slight inflexion up on the curve of specific viscosity of CUP-1 in Figure 4(a). This trend is even more remarkable for CUP-3 when the volume fraction is larger than 0.08. It can be expected that when volume fraction is even higher the electrical double layers will strongly interact and the viscosity will dramatically increase. This phenomenon will be addressed in the future studies.

5. CONCLUSION

This work discussed the rheology behavior of CUPs with different molecular weight, and has at least two findings: first, it was found that the surface water occupies significant volume fraction in CUP suspension and that the thickness of water layer on the surface of CUP shows a trend of increasing with particle sizes. Second, the rheological behavior of CUPs in dilute to semi-dilute ($\phi<0.08$) fit well with Russel's model [26]. The first finding indicate that the CUP can be a good matrix to study the basic properties of surface water since the water layer will give a larger contribution compared with the water on regular colloids such as a latex. Through studying the surface water's property like structure dependence on temperature, pH or salinity, the knowledge can be of vital significance to life science since the surface water plays vital role in the behaviors of many biological components. Also, the large amount of water could impact strongly on the rheological behavior of suspension, which is important in term of its application in coating and adhesives. Since the particle size and charge density of CUP particles can be easily manipulated by controlling the molecular weight and composition of the polymers, it is highly possible to quantitatively study the dependence of rheological behavior of CUPs suspension on particle size or charge densities. That knowledge will help further understanding the electroviscous effect of nanoscale particle. In addition, if the concentration of CUP suspension is so high that the charged particles strongly interact, then the mobility of particles will be highly limited. The possibility of forming a liquid crystal structure will be tremendously increased. Therefore, CUP is an excellent material to study the electrokinetics behavior along with rheology, surface chemistry, even liquid crystallology which can be of fundamental sense to colloid, life and material science.

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II. GEL POINT BEHAVIOR OF COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES

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ABSTRACT

The gel point of a colloidal unimolecular polymer (CUP) aqueous suspension was determined. The zero-shear viscosities of suspensions were measured by capillary viscometer and cone-and-plate rheometer. The relative viscosities were fit to the Krieger-Dough equation $\eta_r = [1 - \frac{\phi}{\phi_{max}}]^{-[\eta]\phi_{max}}$ to determine the maximum packing volume fraction ϕ_{max}. The gel point was found to be much lower than the anticipated random close packing (~0.63) or hexagonal packing (~0.74). The gel point was attributed to the effect of surface water and subsequently the thickness and density of water layer were calculated to be 0.57nm and 1.0688 g/cm^3. The CUP's results were compared with the rheological behavior of commercial waterborne suspensions with particle size 25nm and 77nm. The packing volume fraction of colloids with different particle sizes was predicted considering the effect of surface water.

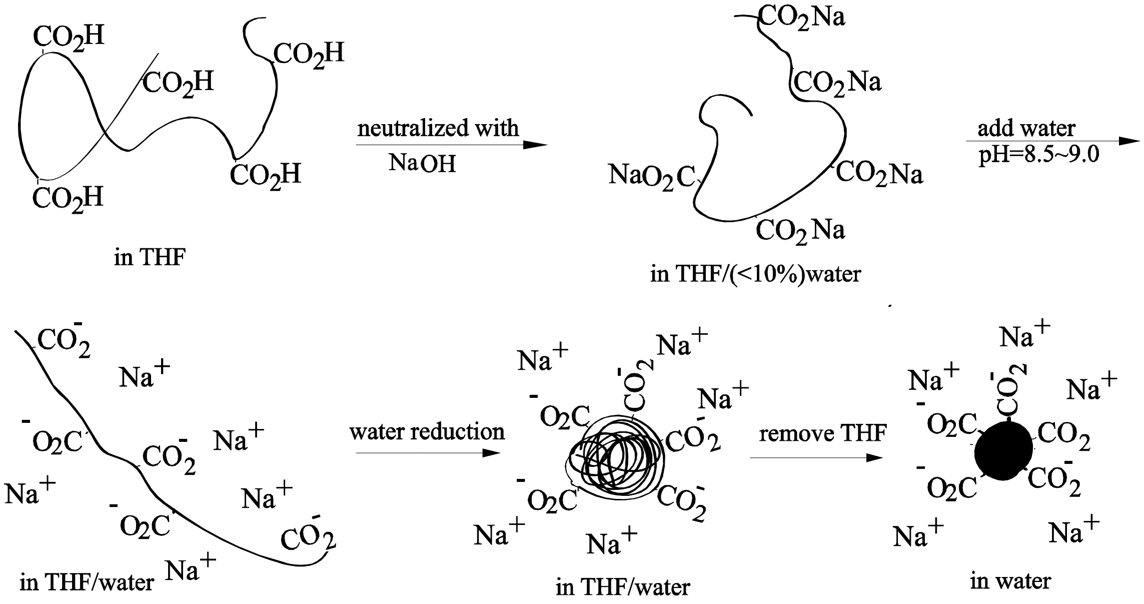
Key words: CUP, Gel point, surface water, random close and hexagonal packing

1. INTRODUCTION

In the waterborne paint industry, the percent solids of a paint has always been a focus from both the quality and the price/cost point. For a regular latex paint, manufactures find it hard to increase the percent solids of a paint higher than 60% without the paint becoming too thick to use. For waterborne urethane, the maximum percent solid is even lower. Formulators have noticed that the solid components of waterborne paint, i.e. resin particles or pigments, increase the viscosity as a function of solids. How the resin or pigment interacts with water and each other is therefore of critical interest. But since latex or waterborne urethane resins contain surfactant or emulsifiers to keep the dispersion stable, it is difficult to apply physical science. The additives in the resins may interfere with any study of the bound or free water. The interaction of a particle with the water produces a layer of water on the particle surface which is different from bulk or free water. The bound or surface water has been suggested to be as thick as from a few water molecules to several dozens of water molecules depending on the surface properties of the particles[1-3].

Colloidal unimolecular polymer particles (CUPs) are a new type of colloid that are formed by the effect of hydrophilic/hydrophobic interaction of the polymer with hydrophilic groups and hydrophobic backbone in the solvent[4-10]. The formation of CUP particles is driven by the polymer-polymer interaction being greater than the polymer-solvent and entropically favored by release of water analogously to micelle formation with hydrophilic or charged groups creating the shape. Scheme 1 shows the process of formation of CUP particles with carboxylate groups on the surface, keeping the particles from aggregation. Once formed these colloidal particles are thermodynamically stable. The CUP suspension contains only charged particles, water and counterions without any additive. Typical CUP particles typically range in size from 2 to 9 nm. These true nanoscale particles make them an excellent material to study the effect that the surface water has on the solids content and the rheology behavior.

Scheme 1. Process of forming CUP from poly(methyl methacrylate-co-methacrylic acid).



About four hundred years ago, Johannes Kepler raised a famous conjecture that no arrangement of equally sized spheres filling a space has a greater average density than that of the cubic close packing (face-centered cubic) and hexagonal close packing arrangements. The maximum packing density is 0.7405, or 74.05% of the volume is occupied by the spheres. After years of effort by many mathematicians and physicists, this conjecture have been proven by Hales[11]. The success in solving the problem of sphere packing can shed light on the gelation problem of suspensions. According to the Kepler conjecture, if the particles in the suspension follow face center cubic packing, volume fraction can reach a maximum of 0.7405; at that point, the suspension will reach maximum density as a solid. In other words, the viscosity of the suspension will reach infinity. Some other lattice packings are often found in physical systems. For example, the maximum volume solid of tetrahedral lattice is 0.3399, cubic lattice is 0.5233, hexagonal lattice is 0.6043. All the packings above are regular types. As to irregular packing, the maximum packing volume fraction is random close packing (RCP). Experiments have shown that RCP at low-limiting shear rate was about 0.63 for sterically stabilized (hard) silica spheres in cyclohexane[12]. Simulation shows RCP is between 0.639 and 0.649[13]. Recent work has analytically shown that the RCP cannot exceed the limit of 0.634[14].

In reality, a homogenous suspension with volume fraction of 0.63-0.74 is really difficult to reach partly because of the difficulty to mix a suspension with so high a viscosity (close to infinity). Another reason is the possibility of aggregation of particles in such high concentration for regular suspensions like latex or colloidal silica. Actually, most of the methods of determining the maximum packing volume fractions for various suspensions were using models relating viscosity and volume fraction and finding out the volume fraction where viscosity reaches infinity. For non-aqueous suspensions, the extrapolated RCP was close to 0.63[12,15,16]. But for aqueous suspensions, the maximum volume fractions were much smaller than 0.63[17,18]. It was attributed to the charge stabilized water layer on the surface of particles. However, due to the limitation of preparing the suspension, such as a latex, there may be residual surfactant even though the latex had been repeatedly dialyzed against deionized water, which was non-trivial when the concentration of suspension is high. It is important to have a suspension that is free of surfactant and is stable even in high concentration.

CUPs neutralized by sodium hydroxide are free of surfactant due to the process of preparation, and it is stable due to its high charge density even in high concentration. As water gradually evaporates from the suspension, the particles approach each other, and the electrostatic repulsion between particles increases. The particles tend to arrange themselves in positions with equal distance from its nearby particles like ions in an ionic crystal. As known, the most stable ionic structure is face-center-cubic, therefore it is reasonable to hypothesize the final structure of CUPs solid is also face-center-cubic. But due to the polydispersity of the CUPs in particle size, it is possible that the maximum packing volume fraction of CUPs suspension is between random close packing, 0.634 and hexagonal close packing 0.7405.

In order to test if CUPs undergo random close packing or hexagonal close packing in water and also discover the properties of bound water on the surface of a particle, the gelation behavior of CUPs was studied. The CUP particles can be treated as macro-ions, or charged hard spheres. Since the CUP particles are just a few nanometers in diameter, their surface area per gram is very large. If the surface has a large amount of “bound water” which is different from bulk water, it will be readily detected. This report discusses the investigation of CUP resins through direct gel point and rheology measurements to determine if there is a “bound water” layer and if the gel point can be predicted. An understanding of the surface water and particle organization in the latter stages of a waterborne particulate resin will aid many researchers in understanding many small particle suspensions at high concentration or during drying.

2. EXPERIMENTAL

2.1 Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. Methyl ethyl ketone, acetone and tetrahydrofuran were purified by distillation. Monomers were purified to remove contaminants and inhibitors. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. All water used was deionized water. Waterborne urethane was supplied by Reichhold, Inc. and the latex by Arkema, Inc. The percent solid of the waterborne urethane is 37.5%, and the density is 1.053 g/ml; the percent solid of latex is 50.2%, and the density is 1.03 g/ml.

2.2 Synthesis and Characterization of Poly(MMA/MAA) Copolymers. Copolymers of MMA and MAA were prepared in a molar ratio of 9:1 by free radical polymerization in methyl ethyl ketone (MEK) and refluxed for 24 hours under argon. AIBN (0.073 mole % to monomers) as the initiator and 1-dodecanthiol as chain transfer agent were used. The un-reacted monomers and solvent were removed in-vacuo. The product was dissolved in distilled acetone and precipitated in de-ionized water. The wet polymer was placed in a 50°C oven and then heated in vacuum to 50°C. The absolute molecular weight of the copolymers was measured using gel permeation chromatography by Viscotek model 305 manufactured by Malvern Corp. Flow rate of THF was 0.5ml/min, and the injection volume 100μl. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight.

2.3 Acid Number. Acid numbers (AN) were measured by the titration method found in ASTM D 974; modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, and phenolphthalein in place of methyl orange.

2.4 Density of Dry Polymer. The density of the dry polymer was measured by a gas displacement pycnometer: Micromeritics AccuPyc II 1340. Volume of sample can be calculated as:

$$V_s = V_c + V_r/(1 - \frac{P_1}{P_2}) \tag{1}$$

where V_s is the sample volume, V_c is the volume of the empty sample chamber, V_r is the volume of the reference volume, P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. The mass was measured by analytical balance.

2.5 Water-reduction. Polymers were dissolved in tetrahydrofuran (THF) (10% w/w) and stirred overnight. Sodium hydroxide was added to neutralize all the acid groups according to its acid number. The same amount of pH modified water (pH=8~9 adjusted by NaOH) to THF was added to the polymer solution by a peristaltic pump at a rate of 1.24g/minute, and the pH of solution was maintained between 8.3 and 9. THF was stripped in-vacuo. Solutions were then filtered through 0.45µm Millipore membrane to remove any foreign materials which was typically measured to be less than 0.05% by weight. The solution was diluted to different concentrations with pH modified water (pH was between 8.3 and 9).

2.6 Shearing Viscosities of CUP Solution. One milliliter of CUP solution was transferred to the well of the Brookfield LV DVIII by Eppendorf pipet. The well's temperature was controlled at 25.0±0.1℃ by circulating constant temperature water bath. Shearing viscosities of CUP under a series of shear rates were measured. The shear rates were programmed to increase at set speed and viscosities were recorded after continuously shearing for 1 minute at each speed.

2.7 Absolute Viscosity of CUP Solution. The CUP suspension was transferred to an Ubbelohde capillary viscometer, which was in a constant temperature water bath at 25.0±0.1℃. The shear rate in the capillary is between $150s^{-1}$ and $3600s^{-1}$ depending on the viscosity of the suspensions. The lower viscosity is, the faster that suspension elute through the capillary, thus the higher shear rate will be. The suspensions were equilibrated for 20 minutes with plastic wrap cover on top of the viscometer to prevent evaporation and CO_2 contamination. A stop watch with 0.01 second precision was used to monitor the elution time. The measurement was repeated at least three times. The estimated standard error was within 0.5%. Absolute viscosity was calculated by Eq. 2

$$\eta = t \cdot d \cdot c \tag{2}$$

where t, d, and c were elution time, density of solution and constants of Ubbelohde with unit second, g/ml and cP/second. The relative viscosity of solution was calculated as

$$\eta_r = \eta / \eta_w \tag{3}$$

where η_w is viscosity of water with unit cP.

2.8 Particle Size of CUP and Distribution. Particle size and distribution were measured by dynamic light scattering instrument Microtrac Nanotrac 250. The viscosity used was that of the suspension due to the high concentration (>8%) and relatively high surface charge on the CUP particle [4-10].

3 RESULTS AND DISCUSSION

3.1 Polymer Characterization. The molecular weight, density, diameter and acid number of CUPs were listed in Table 1. From the acid number, the actual composition of copolymer can be calculated by Eq. 4.

$$\frac{nMMA}{mMAA} = \frac{\frac{56100}{AN} - Mw_{(MAA)}}{Mw_{(MMA)}} \tag{4}$$

If the density of CUP in suspension is assumed to be same as the density of dry polymer, then the theoretical equivalent spherical diameter of CUP can be estimated by $\mathrm{d} = (\frac{6\mathrm{Mn}}{\pi \mathrm{N_A} \rho})^{1/3}$ where M_n is the number average molecular weights, N_A is Avogadro constant, ρ_p is the density of dry polymer. From the measured values of densities and acid number, the calculated diameter and composition for the CUP polymers are listed in Table 1.

3.2 Direct Determination of Gel Point. Instinctually, CUP suspensions will gradually reach the gel point as water in the suspension keeps evaporating as shown in Figure 1. Therefore, attempts were made to concentrate the suspension by placing it in vacuum desiccators with dry sodium hydroxide to minimize CO_2 contamination and remove water. The CUP suspension turned into a solid-like material after several days drying and the weight fraction solids was 44%. However, several issues were found with this method. First, the suspension that underwent evaporation without stirring was not homogenous, so the percent solid of the suspension will give diverse result. Second, as the suspension comes close to its gel point, the water molecules will be slow to evaporate making it difficult to tell when the suspension reaches the true gel point. The direct method was not definitive, therefore a less direct approach using the viscosity increase with volume fraction was used to determine the gel point.

Table 1. Molecular weight, density, diameter and acid number of CUPs.

Mn (kg/mol)	Mw (kg/mol)	Density (g/ml)	d_m[a]	d_c[b]	AN[c]	nMMA/mMAA
111	174	1.2342 ± 0.0018	6.5	6.6	62.2	8.2

a) measured particle size by DLS, nm; b) Calculated particle size from molecular weight, nm; c) Acid number, mgKOH/g polymer

Figure 1. Picture of gelled CUP suspension.

3.3 Viscosity of CUPs. The relative viscosity of suspensions in the high volume fraction range usually follows the Krieger-Dougherty equation[19]

$$\eta_r = [1 - \frac{\phi}{\phi_{max}}]^{-[\eta]\phi_{max}} \tag{5}$$

where ϕ_{max} is the packing volume fraction where viscosity of suspension diverge and $[\eta]$ is the dimensionless intrinsic viscosity of suspension. For non-interacting particles, $[\eta]$ is Einstein's coefficient 2.5, but for charge stabilized particles, it is not necessarily the same. Thus, it is possible that the relative viscosity of suspension at different volume fraction can be fit to the Kriger-Dougherty equation with $[\eta]$ and ϕ_{max} as fitting parameters. Assuming that the viscosity of the suspension reaches infinity when the effective volume fraction of particles, which includes the possible bound layer of water on the surface, reaches random close packing value of 0.634, the thickness of water layer, δ, can be calculated with random close packing and radius of particle by Eq. 6.

$$\phi_{max}(1 + \delta/r)^3 = 0.634 \tag{6}$$

The shear viscosity of CUPs at different volume fractions were measured and plotted in Figure 2 and Figure 3. The volume fraction was calculated by $\phi = \rho_s f/\rho_p$ where ρ_s is density of suspension, f is the mass fraction of the CUP in suspension, and ρ_p is the density of the CUP. The results show that when the volume fraction of the CUP increases, the suspensions show more shear-thinning. This results from the balance between Brownian motion and repulsive force among the CUP particles[20]. When volume fraction of the CUP particles was low, the distance between the CUP particles was so large that the repulsive force interaction was weak, so the Brownian motion dominated, and the suspension presents a random disordered state. As the volume fraction of CUP increased, the repulsive force dominated, so CUP particles form a pseudo-lattice structure, which was unstable under shear.

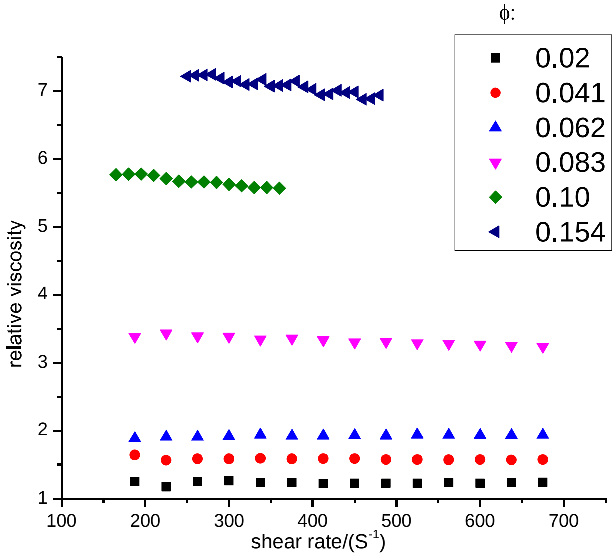


Figure 2. Shear viscosity of CUP with ϕ lower than 0.154.

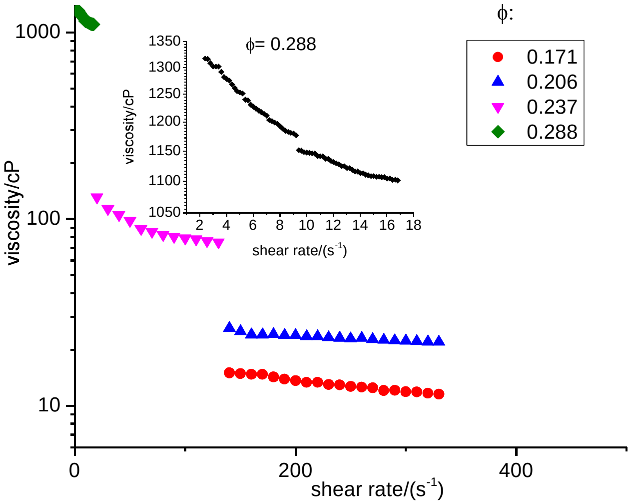


Figure 3. Shear viscosity of CUP with ϕ higher than 0.154.

To further illustrate that point, we fitted the data with Casson's model[21] $\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta_c \dot{\gamma}}$ where τ_0 is the yield stress, the minimum stress to flow, η_c is the plastic viscosity, $\dot{\gamma}$ is the shear rate,τ is the shear stress. From Table 2, it can be seen that when the volume fraction was low (<0.062), yield stress was zero implying that the suspension was a Newtonian fluid. For those suspensions with volume fraction larger than 0.062, the yield stress was larger than zero and keeps increasing with volume fraction indicating that they show more shear-thinning behavior.

Table 2. Fitting result of Casson's model.

ϕ	(τ_0)/Pa	τ_{0error}	(η_c)/cP	η_{cerror}	R^2
0.020	0.000	0.000	1.07	0.00	0.9997
0.041	0.000	0.000	1.33	0.00	0.9987
0.062	0.000	0.000	1.93	0.00	0.9998
0.083	0.029	0.006	3.02	0.00	0.9998
0.100	0.042	0.005	5.07	0.00	0.9998
0.154	0.157	0.031	6.00	0.00	0.9986
0.171	0.240	0.022	7.11	0.21	0.9966
0.206	0.360	0.034	16.40	0.28	0.9986
0.237	0.513	0.026	59.90	0.21	0.9999
0.288	1.010	0.020	946.00	0.51	0.9996

Cross's semi-empirical model[22], Eq. 7, is suitable to estimate the zero-shear viscosity and limiting high shear viscosity where η_r is the relative viscosity of the suspension, $\eta_{r\infty}$ is the limiting high shear relative viscosity, η_{r0} is the zero-shear relative viscosity, τ is shear stress, and b, m are fitting parameters.

$$\eta_r=\eta_{r\infty}+(\eta_{r0}-\eta_{r\infty})/[1+(b\tau)^m] \quad (7)$$

If we fit the relative viscosity and shear rate with Eq. 7 for suspensions with volume fraction between 0.083 and 0.288, we can get the zero-shear viscosity and limiting high viscosity. The fitting results are listed in Table 3.

Table 3. Fitting result of Cross's model.

ϕ	η_{r0}	$\Delta\eta_{r0}$	$\eta_{r\infty}$	$\Delta\eta_{r\infty}$	b	Δb	m	Δm	Adj. R^2
0.083	3.82	0.24	3.28	3.64	1.09E-03	5.71E-03	2.18	8.14	0.9209
0.101	6.50	0.42	6.02	1.42	2.86E-03	3.91E-03	3.15	10.82	0.9339
0.154	8.38	1.85	6.00	3.77	1.16E-03	1.74E-02	1.72	12.52	0.8460
0.171	17.98	0.62	11.92	0.69	4.52E-03	1.70E-04	3.62	0.94	0.9903
0.206	27.36	0.16	24.19	0.40	3.87E-03	1.44E-04	6.05	1.36	0.9851
0.237	178.50	14.95	76.96	2.89	3.20E-02	5.05E-03	1.76	0.30	0.9952
0.288	1506.87	6.42	1186.30	7.72	1.35E-01	2.39E-03	2.12	0.12	0.9963

The dependency coefficients of fitting show that the Cross model was not suitable to suspensions with volume fraction lower than 0.171. In other words, the suspensions with volume fraction higher than 0.171 showed significant shear-thinning behavior.

Compared with charge stabilized poly(styrene-ethylacrylate) particles in water[23] where the suspension did not show obvious shear-thinning up to volume fraction higher than 0.34, the CUP volume fraction was significantly lower. The long-range charge-charge interaction should be able to explain the difference. The effective charges on the surface of CUPs were calculated from Belloni's program[24] at various volume fractions and converted to charge densities which varies between 0.01 and 0.02 C/m^2. It is similar to that of a normal latex particle, normally in the range of 0.01~0.07 C/m^2.[25] However, at same volume fraction, the distance between the smaller CUP particles is much smaller than that of the larger latex particles (inter-particle distance is proportional to diameter of particles). Therefore, a pseudo-lattice structure was more readily formed for the CUP suspensions. This structure was not stable under shearing, so it shows shear thinning behavior. The zero shearing viscosities for suspensions with volume fraction higher than 0.171 were fit from Cross model above. For those suspensions with volume fraction lower than 0.171, the viscosities were measured by Ubbelohde capillary viscometer even though these suepsnions are not strictly Newtonian fluids since these suspensions behaved closer to Newtonian fluid than shear thinning fluids.

3.4 Density and Thickness of Surface Water. As mentioned above, the Krieger-Dougherty equation applies well to zero-shear viscosity of suspensions up to high volume fractions and the fitting result would offer the value of maximum packing volume fraction at the gel point. The relative viscosities of the CUP suspension were plotted against volume fractions, and the data fit with Krieger-Dougherty equation. The fitting result was as shown in Figure 4. From the fitting curve in Figure 4, the fitting parameters ϕ_{max}=0.3940 and $[\eta]$=14.1 were obtained. The value of intrinsic viscosity was similar to spherical polyelectrolytes[26] which are highly charged indicating that the surface of CUPs was also highly charged. The value of ϕ_{max}=0.3940 was surprisingly low compared with other reported maximum packing volume fractions[12]. But recall that there was the possibility of a large amount of bound or surface water. For further calculation, we made two assumptions: first, the CUPs are spherical and the surface water forms a homogeneous layer on the spherical CUP particle; second, the CUP particles, along with the surface water reach random close packing when the actual volume fraction of CUP is 0.394. Thus, the thickness of water layer was calculated to be $\delta=\left(\sqrt[3]{\frac{0.634}{0.394}}-1\right)\times 3.3=$ 0.57nm from Eq. 6.

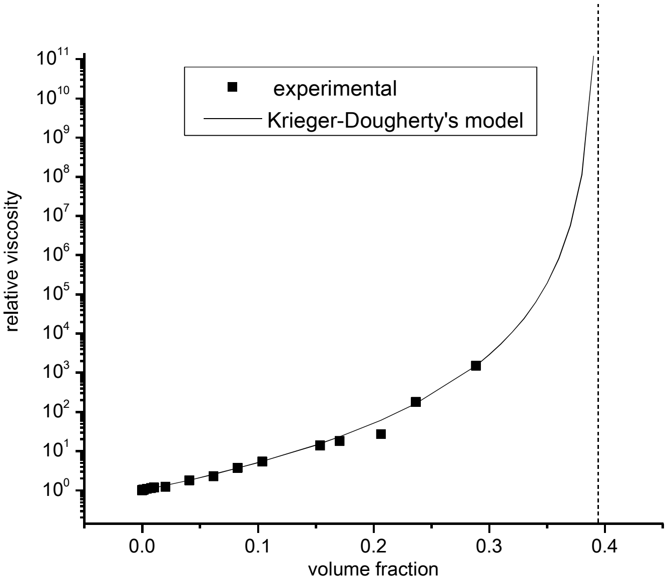


Figure 4. Zero-shear viscosity of CUP versus volume fraction and fitting curve of Krieger-Dougherty equation.

If we assume that the particle was in the random close packing and that the actual particle and the bound or surface water was as depicted in Figure 5, then the volume fraction of surface water will be 0.634-0.3940=0.24. The volume fraction of free water between particles is 1-0.634=0.366. Assuming 1 ml suspension of the CUP, the densities should be related as follows:

$$\rho_p \Phi_p + \rho_{H_2O,B} \Phi_{H_2O,B} + \rho_{H_2O,S} \Phi_{H_2O,S} = \rho_s \tag{8}$$

where ρ_s is the density of suspension, ρ_p is the density of the CUP, $\rho_{H_2O,S}$ is the density of surface water, ϕ_p is the volume fraction of the CUP, $\Phi_{H_2O,S}$ is the volume fraction of surface water, $\Phi_{H_2O,B}$ is the volume fraction of bulk water. The density of the suspension at the gel point was extrapolated by the relation between measured volume fractions (from zero to 0.1) and densities. It was 1.1077g/ml.

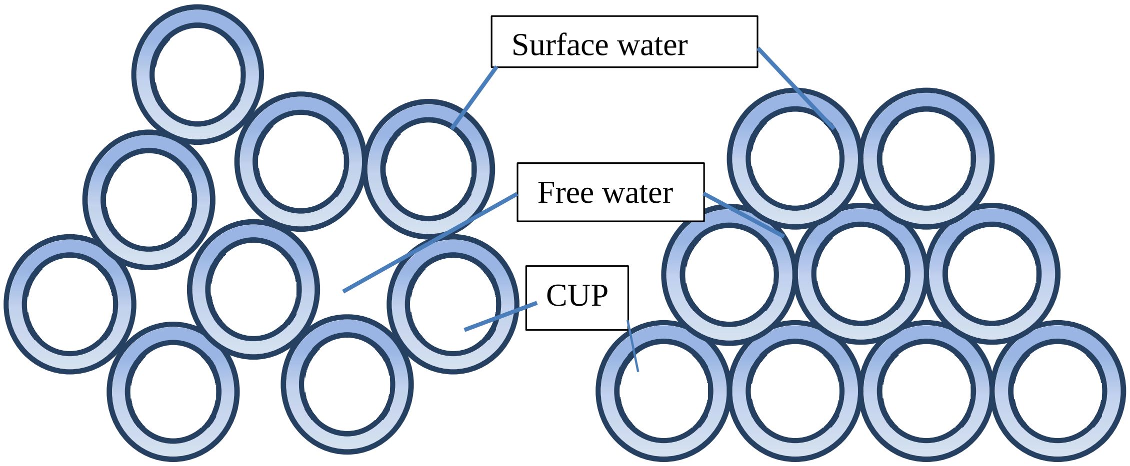


Figure 5. Random close packing of CUP with surface water (left); Kepler Conjecture with CUP and its surface water (right).

Replacing each term with the corresponding value, the density of surface water was 1.0688g/ml, which was 7.19% larger than that of bulk water at 25°C. Therefore, the water on the surface of the particles was more compact than bulk water. We can simply verify the validity of the density and thickness of water layer by the simple arithmetic calculation based on the relationship between surface water, bulk water and particle volume fraction. Still, the summation of volume fraction of CUP particle, surface water, and bulk water is one. That is Eq. 9.

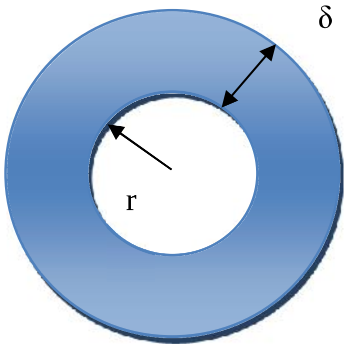


Figure 6. CUP particle and its surface water.

$$\Phi_p + \Phi_{H_2O,B} + \Phi_{H_2O,S} = 1 \tag{9}$$

Also there exists a conservation of mass of total material as Eq. 10

$$m_s = m_p + m_{H_2O,S} + m_{H_2O,B} \tag{10}$$

where

$$m_p = \rho_s f \tag{11}$$

$$m_{H_2O,S} = \rho_{H_2O,S} \Phi_{H_2O,S} \tag{12}$$

$$m_{H_2O,B} = \Phi_{H_2O,B} \rho_{H_2O,B} \tag{13}$$

and *m* denotes mass of each material. Using Eq. 10 through 13, along with the relation between volume fraction of particle and surface water, which is Eq. 14, Eq. 9 can be solved, and we get $\frac{1}{\rho_s} = kf + b$ where $b = \frac{1}{\rho_{H_2O,B}}$ and $k = \frac{\left(1+\frac{\delta}{r}\right)^3}{\rho_p} - \frac{1}{\rho_{H_2O,B}} - \frac{\rho_{H_2O,S}}{\rho_p \rho_{H_2O,B}}[\left(1+\frac{\delta}{r}\right)^3 - 1]$.

$$\Phi_{H_2O,S} = [\left(1+\frac{\delta}{r}\right)^3 - 1]\,\Phi_p \qquad (14)$$

Then we measured densities (ρ_s) at various mass fraction (f) of CUP suspension, and plot $\frac{1}{\rho_s}$ against *f* as shown in Figure 7.

As shown in Figure 7, the reciprocal of density of CUP was a linear function of mass fraction of CUP particles. From the curve, the slope of curve

$$k = \frac{\left(1+\frac{\delta}{r}\right)^3}{\rho_p} - \frac{1}{\rho_{H_2O,B}} - \frac{\rho_{H_2O,S}}{\rho_p \rho_{H_2O,B}}[\left(1+\frac{\delta}{r}\right)^3 - 1] = -0.2282. \qquad (15)$$

If we plug in δ=0.57nm and $\rho_{H_2O,S}$=1.0688 g/ml which are calculated thickness and density of water layer, then the left side of Eq. 15 will be equal to -0.22845. The value is off by only 0.11% from the measured value -0.2282. The conclusion that the thickness and density of bound water was 0.57nm and 1.0688g/ml has a good fit in the dilute regime.

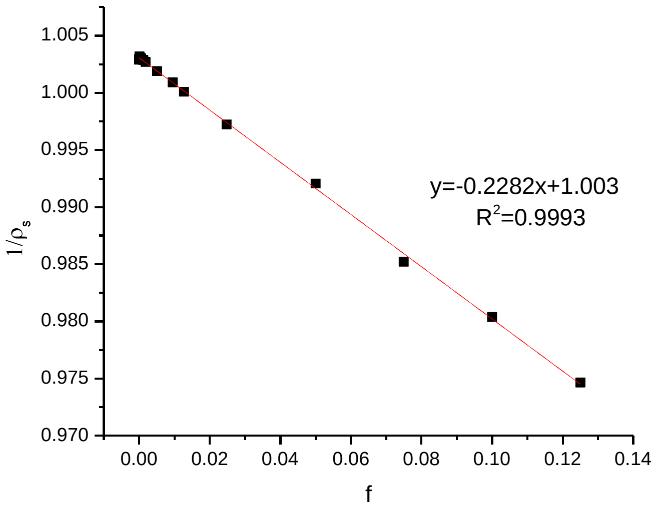


Figure 7. Dependence of $1/\rho_s$ on weight fraction of CUP.

The high density of surface water was found to exist on the surface of protein. Chen[27] reported that the maximum density of first hydrated layer on protein ranging from 0.21nm to 0.33nm from the surface of protein was six times of that of water at 277K. Based on the radial distribution of density of hydrate water, the calculated average density is 44.5% larger than the density of water at 277k. The density of second hydrated layer, extending from 0.33 to 0.50nm is much lower with average density being 43% of the density of water at 277k. In terms of the density of surface water on CUPs, it is possible that there exist similar surface water layers with different densities.

If one water molecule's diameter is 0.28nm, then there will be approximately 2 layers of water surrounding each CUP particle. The value of 0.57nm is consistent with the result of Davies and Rideal[28] who estimated the shear plane was of order 0.3nm from the plane of head group of a surfactant stabilized oil-in-water emulsion system. The shear plane was considered as a zone where the relative velocity of dispersing medium to solid surface is zero. In other words, the viscosity in the shear plane is approaching infinity. Generally, the average thickness of shear plane is in the order of several molecules. In a salt free suspension, the value of Debye length, κ^{-1}, is determined by the counterion dissociated from charged group and the background ionic strength resulting from the base used to control the pH value of the suspension and can be presented as Eq. 16.

$$\kappa^{-1} = 1/\sqrt{\frac{e^2}{\varepsilon_0\varepsilon_r k_B T}(nZ_{eff} + 2000N_A \cdot 10^{pH-14})} \tag{16}$$

where e is elementary charge, ε_0 is vacuum permittivity, ε_r is relative dielectric constant of water, k_B is Boltzmann constant, T is temperature, n is number density of CUPs in suspension, expressed as the ration of volume fraction of CUP to the volume of a single particle, Z_{eff} is effective charge calculated from Belloni's program[24], N_A is Avogadro constant, pH is the pH value of suspension. When the volume fraction of CUPs is 0.394 at gel point, the number density n is 2.74×10^{24} /m^3, and the effective charge was calculated to be 31. Thus, at pH=8.5 suspension, the κ^{-1} is calculated be 1.2nm. Therefore, the calculated 0.57nm of water layer on CUPs is consistent with the position of shear plane of the CUPs.

It should be noted that the hydrophobic part of the CUPs can also adsorb up to 2% w/w of water[29,30]. However, the volume of adsorbed water only counts for 2.46% increased volume of the CUPs. (the density ratio of CUPs to water is 1.23). For CUP particles with a 3.3 nm radius, the additional volume fraction by surface water was ~61% of the CUP particle volume itself. Therefore, it can be concluded that most of the bound water is located on the surface of CUPs.

For common resin particles, like a latex with a radius of 100 nm, if the thickness of surface water is the same, the ratio of surface water to latex by volume is only 1.72%. Figure 8 shows the calculated volume fraction of particles at gel point as a function of their particle size and thickness of bound water layer. Figure 8 shows that both size and thickness of bound water have significant effect on maximum volume fraction. For particles with same thickness of bound water, ϕ_{max} drops dramatically with particle size, especially for particles with a thicker water layer. For particles with the same size, the thicker the bound water layer is, the smaller ϕ_{max} will be. This effect is more significant for smaller particles than for a large particle.

To illustrate the effect of particle size on the viscosity, the viscosity behavior of commercial waterborne urethane and latex were measured with increasing volume fractions and presented in Figure 9. The particle size of waterborne urethane was measured to be 25nm, and the latex 77nm. The intrinsic viscosities of waterborne urethane and latex were measured to be 8.0 and 5.5 respectively in term of volume fraction by relating relative viscosity with volume fraction[19] as Figure 10. Assuming that the thickness of water layer on the surface of waterborne urethane and latex are all 0.57nm, then the ϕ_{max} for waterborne urethane and latex are 0.55 and 0.6 respectively according to Eq. 6. The theoretical relative viscosities of waterborne urethane and latex can be predicted by Eq. 17 and 18 in form of Krieger-Dougherty's equation where subscript 1 and 2 denote waterborne urethane and latex respectively. The predicted relative viscosities were plotted in Figure 9.

$$\eta_{r1} = (1 - \frac{\phi}{0.55})^{-[\eta]_1 \times 0.55} \tag{17}$$

$$\eta_{r2} = (1 - \frac{\phi}{0.60})^{-[\eta]_2 \times 0.60} \tag{18}$$

As shown in Figure 9, at same volume fraction, the viscosity of the CUPs is always larger than those of waterborne urethane and latex. The rheological behavior agree quite well with the hypothesis that the surface water has more effect on rheology of smaller particle than that of larger particles if the thickness of water layers is close. The deviation of experimental results from the predicted values at high concentration can be attributed to the unknown surface structure or the residual like surfactants or rheological modifiers. This again shows the advantage of CUP's being used as model material to study gel point behaviors of charged particle: no interference from residuals.

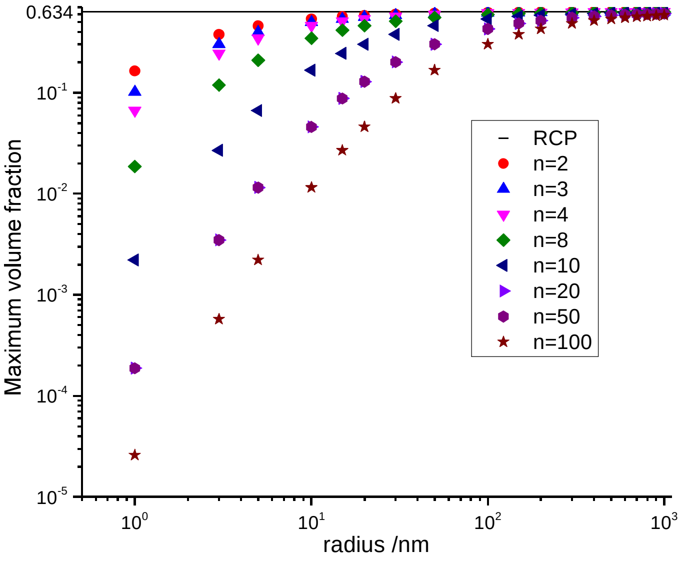


Figure 8. Calculated maximum volume fraction related with particle size and thickness of bound water. (n is number of water layers)

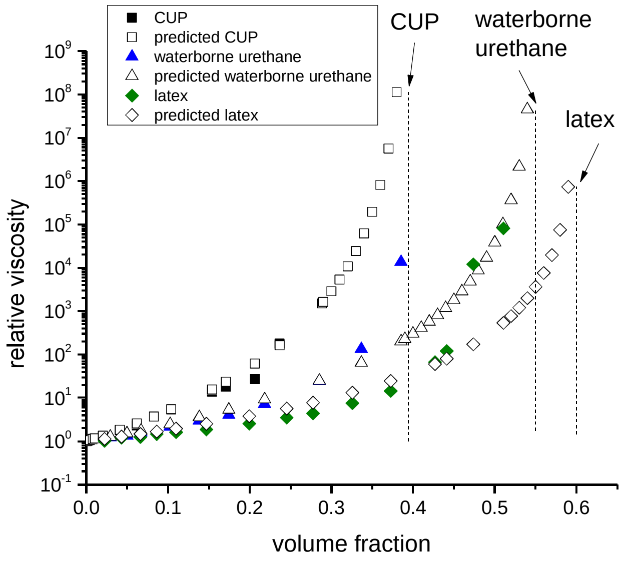


Figure 9. Relative viscosities of CUP and commerical waterborne resin. Open symbols stand for the predicted viscosities from Krieger-Dougherty's equation. Dash lines denote the maximum packing volume fraction, RCP, for each particle.

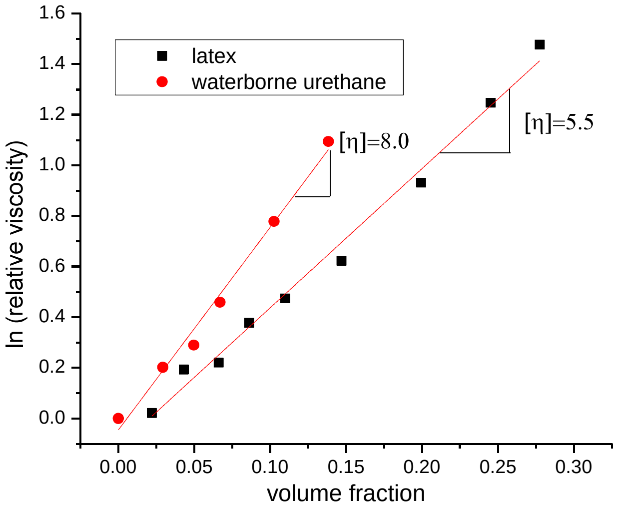


Figure 10. ln ηrel~ϕ for waterborne urethane and latex.

4. CONCLUSION

The viscosities of the CUP suspension measured from capillary viscometer and rheometer were fit into Krieger-Dougherty's equation, from which the maximum volume fraction for CUP was obtained. Based on that relationship and the random close packing assumption, the density and thickness of water layer surrounding the CUP particle was calculated. This finding implies that the surface water can play a major role in the rheology behavior of the colloid when the dispersed particle was small. The primary effect was due to the surface charge causing particle particle repulsion and secondly created a layer of water on the surface of the particle. This water layer was denser than bulk water by 7.19%. When the effect was analyzed, the gel point will decrease in solids content as the particle size decreases at constant ionic charge density. If the density of the particle surface charge changes, for example becoming larger, the water layer would be expected to increase in thickness. For simple latexes a 0.56 nm thick water layer contributes less than 2% but for particles the scale of CUP, the effect becomes dominant. In practice, when we need to estimate the rheological behavior of an unknown suspension with charged stabilized particle at high concentration, we can first estimate its maximum packing volume fraction by Eq. 6 assuming that there is a specific number of layers of water on the surface. Once the intrinsic viscosity of the suspension is determined, the relative viscosity can be estimated by Eq. 5. In addition, CUP will be an excellent model material to study the physical and chemical properties of surface water and extend that knowledge to life or biology science since the surface water on proteins play important role in its activity. When the water in CUP suspension gradually evaporate, the CUP particle should approach random close packing with the volume fraction of CUP itself being 0.63, similar to the regular particle like silica[12]. The question is, can the CUPs continue to organize and reach hexagonal close packing? The latex particles cannot organize into HCP without external disturbance since the Brownian motion of water molecules is not strong enough to move the particles to its most compact form. But since the CUP particle is so much smaller, it should be possible for Brownian motion to "shake" them to a position where the electrostatic repulsion and Brownian motion balance and the system reach its most stable structure. Therefore, CUPs may arrange hexagonal close packing as they move from the initial gel point to a dry solid. This will be the topic of future work.

5. ACKNOWLEDGMENTS

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III. SURFACE TENSION OF COLLOIDAL UNIMOLECULAR POLYMER PARTICLES AT THE N_2/WATER INTERFACE

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ABSTRACT

The surface tension of 3-9 nm Colloidal Unimolecular Polymer (CUP) suspensions at the air/water interface were measured as a function of concentration and molecular weight. The surface activities of the CUP particles were found to relate with the molecular weight of polymer. These nano scale particles, 3-7nm in diameter, follow the size distribution of the GPC absolute molecular weight. The surface charge density of these particles was based upon the acid content of the resin. The relationship between size and surface tension was found to be different from that of latex, polyelectrolytes and silica particles. The high surface charge density of the particles and their small size may produce the effect.

1. INTRODUCTION

Over the past two decades, the surface behavior of small charge stabilized colloid suspensions without other surface active ingredients have been widely studied. These suspensions include silica[1], polystyrene[1], titanium dioxide[2], etc. Paunev[3] has developed a relationship for the adsorption of charged colloidal particle at air-water interface. Although the study addressed the case for large (particle size larger than 30nm), low surface potential (zeta potential lower than 25mv), it sheds light on the possible factors that affect the adsorption of charged particles on the water-air surface. These factors are charge density, particle size, temperature, electrolyte concentration, contact angle and surface tension of particle on water-air phase. Since the adsorption isotherm, Γ, can be expressed as[4]

$$\Gamma = -\frac{a_2}{\mathrm{RT}}\frac{d\gamma}{da_2} \tag{1}$$

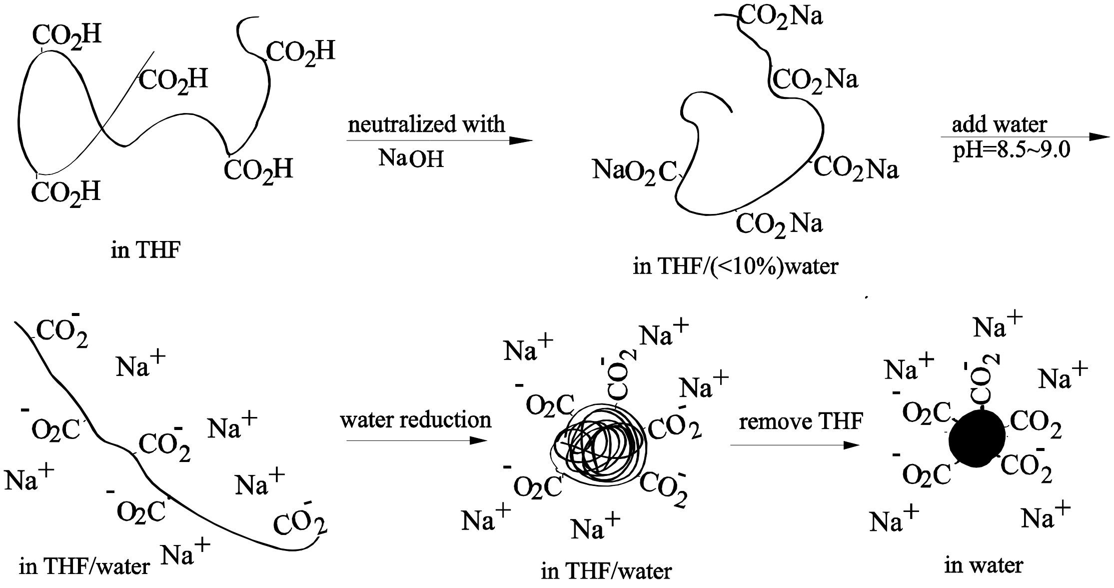
where a_2 is the activity of the solute, R is the gas constant, T is the absolute temperature, it is possible to relate surface tension behavior of suspensions to the previous factors.

Studies on the surface tension behavior of truly nanoscale (particle size smaller than 10 nm) charge stabilized particles has been seldom reported partly due to the difficulty in making a stable dispersion containing only nanoscale particles without other ingredients, except for some nanoscale inorganic particles like silica[1, 5], bismuth telluride nanoparticles[6] and fullerene dispersed in toluene[7]. But charge stabilized silica doesn’t show much surface activity[1, 5]. Fullerene shows some interesting surface activity in toluene and benzene.[7]

The introduction of colloidal unimolecular polymer particles (CUPs)[8] offers an easy method for the preparation of “clean” and stable dispersions with nanoscale charge stabilized particles whose composition and particle size are easily controlled. CUPs are formed by the effect of hydrophilic/hydrophobic interactions of the polymer with a change in the solvent. The formation of CUP particles is driven by the polymer-polymer interaction being greater than the polymer-solvent interaction and entropically favored by release of the water analogously to micelle formation with hydrophilic or charged groups creating the sphere-like shape. Scheme 5.1 shows the formation of CUP particles with carboxylate groups on the surface, keeping the particles from aggregation. Once formed these colloidal particles are thermodynamically stable.[9] The CUP suspension contains only charged particles, water and counterions.

This study will focus on the surface tension behavior of CUPs aiming at development of the knowledge of possible factors that affect the surface tension behavior so as to offer fundamental information for possible application such as coatings.

Scheme 1. Process of Forming CUP particles from poly(methyl methacrylate-co-methacrylic acid).



2. EXPERIMENTAL

2.1 Materials and Purification. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. Methyl ethyl ketone and acetone was purified by drying with anhydrous magnesium sulfate followed by simply distillation. Tetrahydrofuran was dried and distilled same with methyl ethyl ketone, but under the protection of nitrogen or argon gas during distillation. MMA was removed of inhibitors by mixing with 10% sodium bicarbonate, and then rinsed twice with deionized water followed by rinsing with brine twice. Then MMA was dried with magnesium sulfate, filtered, and distilled with presence of copper bromide and protection of nitrogen or argon gas. MAA was distilled with presence of copper bromide under vacuum. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Deionized water was used for all experiments.

2.2 Synthesis of Poly(MMA/MAA) Copolymers. MMA and MAA monomers were placed in a 500ml round bottom flask with a molar ratio of 9:1 in methyl ethyl ketone (MEK). The ratio of monomer to MEK is 1:2 by weight. The mixture was refluxed for 24 hours under argon with AIBN (0.073 mole % to monomers) as the initiator and 1-dodecanthiol as chain transfer agent. The un-reacted monomers and solvent were removed by reduced pressure. The products were precipitated in de-ionized water under mixing of high speed disperser. The wet polymer was placed in a 50°C oven to remove most of the water and then heated in vacuum to 50°C for 24 hours.

2.3 Absolute Molecular Weight of Copolymers. The absolute molecular weight of the copolymers and distribution was measured using gel permeation chromatography by Viscotek model 305 manufactured by Malvern Corp. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight. Flow rate of THF was 0.5ml/min, and the injection volume 100μl.

2.4 Acid Numbers (AN). The acid numbers of copolymers were measured by the titration method found in ASTM D 974; modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, and phenolphthalein in place of methyl orange. The titration was performed in tetrahydrofuran as the solvent.

2.5 Preparation of CUPs Suspension. The copolymers systhesized were dissolved in tetrahydrofuran (THF) (10% w/w) and stirred overnight. Acid groups of the copolymer were neutralized by sodium hydroxide according to its acid number. The equal amount of pH modified water (pH=8.5~9 adjusted by NH_4OH) to THF was added to the solution by a peristaltic pump at a rate of 1.24g/minute with the tip of tubing inside the solution. The pH of solution was maintained between 8.5 and 9. THF was then stripped in-vacuo. Solutions were then filtered through 0.45μm Millipore membrane to remove any foreign materials which were typically measured to be less than 0.05% by weight.

2.6 Density of Dry CUP Particles. The suspensions of CUP were dried in vacuum oven heated at 50℃ in presence of solid sodium hydroxide to absorb carbon dioxide. The sample, clear crystal-like material was then heated at 110℃ to constant weight. The density of the dry cup was measured by a gas displacement pycnometer: Micromeritics AccuPycII 1340. Volume of sample can be calculated as:

$$\mathrm{V_s} = \mathrm{V_c} + \mathrm{V_r}/(1 - \frac{\mathrm{P_1}}{\mathrm{P_2}}) \tag{2}$$

where V_s is the sample volume, V_c is the volume of the empty sample chamber, V_r is the volume of the reference volume, P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. Equilibrium flow rate of Helium gas is 0.005psig/min, temperature was controlled at 25.89±0.04℃. Twenty five readings were made for each sample, and the results were reported by its average and standard deviation.

2.7 Particle Size Analysis. The particle sizes of CUPs were determined by dynamic light scattering (DLS) with Nanotrac 250 manufactured by Microtrac. The suspension's viscosity was entered to calculate particle size.

The densities of suspensions were measured by piconometer. The suspensions were diluted to series concentration by Milli-Q ultrapure water with resistance being 18.3 MΩ. The concentrations were calculated with $\mathrm{c} = 10^6 \times \frac{f}{\rho_s Mn}$ where c is concentration with unit mol/m^3, f is weight fraction, ρ_s is density of suspension with unit g/ml, and Mn is the average molecular weights of polymer by number with unit g/mol.

2.8 Surface Tension of CUP Suspensions. Sensadyne QC-6000 was used to measure the surface tension of CUP suspensions. Suspensions were equilibrated in a constant temperature water bath at $25\pm\mathbf{0.1}$℃ before measuring. The tensiometer was calibrated with analytical reagent methanol and Milli-Q ultrapure water with resistance of 18.3 MΩ. Temperature of thermo couple of tensiometer was calibrated with two known temperatures. Flow rate of nitrogen gas was 40ml/minute and flow pressure was maintained at 25 psi.

3. RESULT AND DISCUSSION

3.1 Characterization of Polymers. The molecular weight, acid number and densities of the copolymers are listed on Table 1. It shows that the composition of the copolymers had similar acid numbers. The densities of dry CUP increase with increasing molecular weights as expected since the weight fraction of end groups decreased with increasing molecular weight.

Table 1. Molecular weight, acid number and densities of copolymers.

Sample ID	Mn (kg/mol)	Mw (kg/mol)	AN[a]	ρ_p[b] (g/ml)
Polymer 1	15	24	57.3	1.2257±0.0007
Polymer 2	28	35	59.1	1.2246±0.0018
Polymer 3	36	45	57.7	1.2326±0.0015
Polymer 4	111	174	62.0	1.2342±0.0018

a)Acid number from ASTM D 974, mgKOH/g b) Density of dry CUPs at 25.89 ± 0.04℃ except polymer 1 at 24.38 ± 0.03℃.

3.2 Particle Size Analysis. The particle size of CUP was measured by Microtrac Nanotrac 250 by dynamic light scattering. The instrument first measured the diffusion coefficient of particle in the media, then calculated the particle size by the Stokes-Einstein equation $\mathbf{D} = \frac{\mathbf{k_B T}}{\mathbf{6\pi\eta r}}$ where D is the diffusion coefficient, kB is the Boltzmann constant, T is the absolute temperature, r is the radius of the particle, η is viscosity of the solvent. In this study, since the concentration of suspension was high, roughly 10%, the viscosity of suspension was used instead of the solvent due to the correction of general

Stokes-Einstein equation10. The result was presented in Table 2. The results show that the measured number average diameters were similar to calculated diameter from number average molecular weight. The polydispersity of the chains by GPC also matched the size distribution by DLS.

Table 2. Particle size and molecular weight of CUP.

sample ID	Mn (kg/mol)	d(DLS)[a] nm	d(GPC)[b] nm
CUP-1	16	3.4	3.5
CUP-2	28	4.2	4.2
CUP-3	36	4.6	4.5
CUP-4	111	6.5	6.6

a) Diameters measured by dynamic light scattering

b) Diameters estimated by average molecular weight using GPC by $d = \sqrt[3]{\frac{6M_n}{\pi N_A \rho_p}}$

3.3 Surface Tension Measurement. There are many methods of measuring the surface tension of suspensions such as ring method11, oscillating jet method12, drop methods13, maximum differential bubble pressure method14. In this study, the maximum bubble pressure method was used because it has several advantages. First, the measurement was done inside the dispersion, so the effect of humidity, air turbulence, and contamination of carbon dioxide were avoided. Second, the operation and cleaning after testing was easier. The method can measure both dynamic and static surface tension of suspension as long as the surface age was properly controlled through adjusting the bubble rate. In this study, only the static surface tensions were measured.

Figure 1 presents the surface tension behavior of CUPs with different molecular weights at different concentrations. As expected, all surface tension of suspension decreased with increasing concentration of CUP. When the concentration of CUPs approach infinite dilution, the surface tension of suspension approaches water's surface tension,72.08 dynes/cm. The behavior was similar to a solution of surfactant before reaching the critical micelle concentration where the surface tension keeps decreasing[15]. More interestingly, there exists a difference in the surface activity. The surface tension versus concentration was fitted with a linear equation, the results were shown in Table 3.

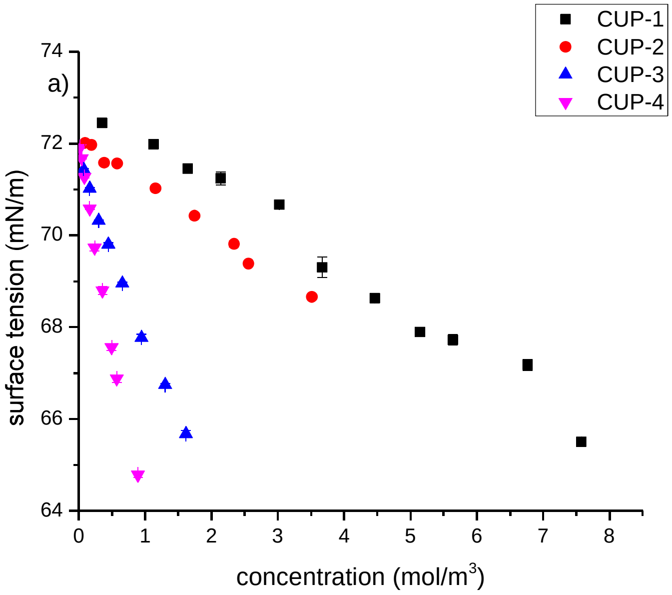


Figure 1. Surface tensions of CUP suspension as a function of concentration. a) linear scale; b)semi-log 10 scale.

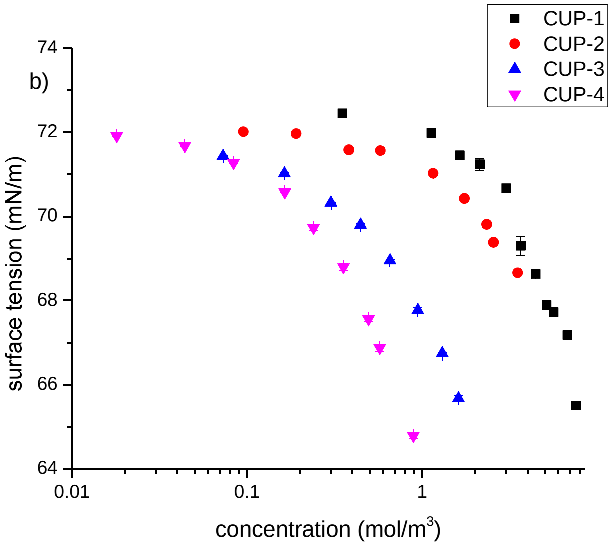


Figure 1. Surface tensions of CUP suspension as a function of concentration. a) linear scale; b)semi-log 10 scale. (Cont.)

Table 3. Fitting result of surface tension versus concentration.

Sample	d(nm)	dγ/dc	Δdγ/dc	intercept (b)	Δb	Adj. R^2
CUP-1	3.4	-0.978	0.032	73.06	0.12	0.989
CUP-2	4.2	-0.979	0.036	72.09	0.04	0.989
CUP-3	4.6	-3.802	0.122	71.58	0.07	0.993
CUP-4	6.5	-8.555	0.212	72.02	0.04	0.995

The fit was very good to a linear equation. Note that the intercepts b for all the suspensions were all close to water's surface tension at 25℃, 72.08 dynes/cm. Therefore a simple linear equation containing surface activity as the slope and water's surface tension as the intercept can be used to describe the surface tension of CUP suspension. That is,

$$\gamma - \gamma_w = k\mathrm{d}\gamma/\mathrm{dc} \tag{3}$$

where γ is surface tension of CUP suspension, γ_w is surface tension of water at 25°C, k is the slope of the plot.

To further calculate the surface excess of the suspension, the relation between surface tension and activity of CUP suspension should be determined. When the particle is neutral and dilute, the activity can be approximated as concentration. But for charged particles, the relation between concentration and activity should be corrected with mean activity coefficient $f_\pm$. According to Debye-Hückel equation[16], the mean activity coefficient of a solute in water at 25°C can be expressed as equation 4:

$$log f_\pm = -\frac{0.5115|Z_1 Z_2|\sqrt{I}}{1+3.291\times10^7 r\sqrt{I}} \quad (4)$$

where Z_1 and Z_2 are charge number of the macroion and its counterion, r is the effective radius the of charged particle with unit cm, I is ionic strength of the suspension in mol/L. In a salt-free suspension, the ionic strength of suspension is determined by the dissociated counterion and the ions in the reservoir such as the hydroxide, hydronium, and sodium ions disassociated from added sodium hydroxide. If the effective charge number of each CUPs is Z_{eff}, i.e. each particle disscociates Z_{eff} counterions, then the ionic strength I can be expressed as

$$I = \frac{1}{2}(cZ_{eff} + 2 \times 10^{pH-14}) \quad (5)$$

where c is the concentration of CUPs in mol/L. The first term in right side of Equation 5 denote the contribution of counterions from CUPs to the ionic strength, and the second term is from added sodium hydroxide which is used to maintain the constant pH of suspension. Since the pH is maintained at 9~10, the concentration of hydronium was negligible compared with hydroxide. Due to counterion condensation and dissociation equilibrium, the value of effective charge can be significantly lower than its bare charge.

With the aid of a program supplied by Belloni[17], the effective charges are calculated at each concentration for each CUPs. The calculated Z_{eff}, ionic strength, mean activity coefficient and activity were listed on Table 4.

Table 4. Calculated effective charge, ionic strength, activity coefficient and activity of CUPs at different concentration.

polymer	c^a	Z_{eff}	I^b	$f_{\pm}$	a^c	σ^e	r_s^f
1	7.575	7.7	2.92E-02	0.45	3.431	25.3	2.8
	6.766	7.8	2.64E-02	0.46	3.096	42.7	3.7
	5.639	8.1	2.29E-02	0.46	2.582	165.4	7.3
	5.142	8.2	2.11E-02	0.46	2.372	103.7	5.7
	4.462	8.3	1.85E-02	0.47	2.096	86.6	5.3
	3.667	8.6	1.58E-02	0.47	1.737	71.8	4.8
	3.023	8.8	1.33E-02	0.48	1.462	84.1	5.2
	2.138	9.1	9.74E-03	0.51	1.082	294.4	9.7
	1.643	9.4	7.72E-03	0.52	0.856	328.9	10.2
	1.127	9.8	5.52E-03	0.55	0.615	399.4	11.3
	0.350	10.8	1.89E-03	0.64	0.224	896.0	16.9
2	3.514	17.5	2.29E-02	0.32	1.133	165.9	7.3
	2.557	18.3	1.74E-02	0.33	0.847	108.0	5.9
	2.340	18.4	1.62E-02	0.33	0.779	109.3	5.9
	1.744	19.0	1.25E-02	0.35	0.603	199.5	8.0
	1.155	19.7	8.62E-03	0.37	0.428	304.5	9.8
	0.577	20.8	4.57E-03	0.42	0.245	810.0	16.1
	0.381	21.4	3.14E-03	0.46	0.175	1107.3	18.8
	0.191	22.3	1.65E-03	0.53	0.100	1071.1	18.5
	0.095	23.2	8.68E-04	0.60	0.057	5498.5	41.8
3	1.615	25.8	1.38E-02	0.29	0.461	69.4	4.7
	1.303	26.3	1.14E-02	0.30	0.386	82.7	5.1
	0.946	26.9	8.53E-03	0.32	0.299	100.7	5.7
	0.655	27.5	6.07E-03	0.34	0.225	117.4	6.1
	0.444	28.1	4.23E-03	0.38	0.168	180.1	7.6
	0.301	28.7	2.96E-03	0.41	0.124	256.8	9.0
	0.163	29.5	1.67E-03	0.47	0.078	385.1	11.1
	0.073	30.7	7.87E-04	0.56	0.041	638.9	14.3

Table 4. Calculated effective charge, ionic strength, activity coefficient and activity of CUPs at different concentration.(Cont.)

4	0.890	42.7	1.90E-02	0.061	0.054	48.5	3.9
	0.572	43.5	1.25E-02	0.074	0.042	48.6	3.9
	0.495	43.8	1.08E-02	0.079	0.039	51.8	4.1
	0.355	44.3	7.88E-03	0.093	0.033	67.1	4.6
	0.239	44.9	5.39E-03	0.110	0.027	87.7	5.3
	0.164	45.5	3.74E-03	0.140	0.023	124.5	6.3
	0.084	46.5	1.96E-03	0.19	0.016	255.1	9.0
	0.044	47.4	1.05E-03	0.26	0.011	510.2	12.7
	0.018	48.8	4.49E-04	0.37	0.007	945.4	17.4

a) Concentration, mol/m^3;b) ionic strength, mol/L; c) Mean Activity, mol/m^3; d) Surface excess, 10^{-6} mol/m^2; e) area occupied per particle on the surface, Ȧ^2.f) radius of circle occupied by each CUP particle, Ȧ

It was expected that the effective charge Z_{eff} decreases with concentration due to counterion condensation. Table 4 also shows that $f_{\pm}$ deviated significant from unity especially for CUP-4 at high concentration, which illustrated the necessity of activity correction. The surface tension and activity of suspension were plotted for each CUP as Figure 2.

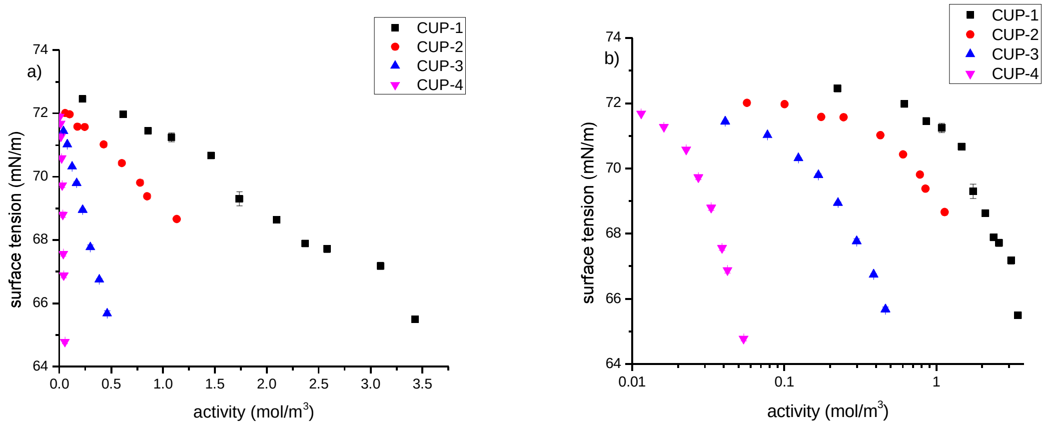


Figure 2. Surface tensions of CUP suspension as a function of activity. a) linear scale; b) semi-log 10 scale.

In Figure 2.b, it is remarkable that the surface activity of CUPs increased with molecular weight in terms of the order of critical concentration where the surface tension started to change significantly. The CUPs particle can be considered as an aggregate of sodium carboxylates, which are surface active in reducing the surface tension of water. At same molar concentrations, larger CUP particles have larger amount of carboxylate groups so that can reduce more surface tension of water.

In Figure 2, the values of $\partial\gamma / \partial\ln(a)$ at each point were calculated from the curve, and surface excess $\Gamma = -\frac{1}{RT}\frac{\partial\gamma}{\partial\ln(a)}$ were evaluated. The surface excess of suspensions were plotted against activities in Figure 3.

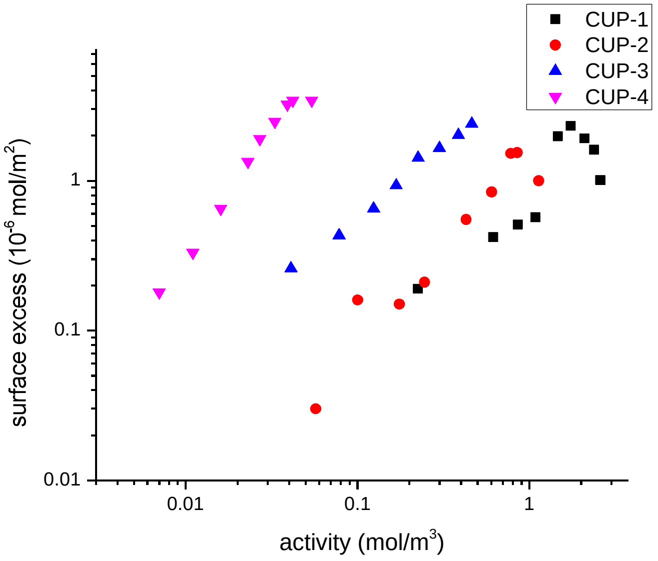


Figure 3. Surface excess as a function of activity for CUPs.

Figure 3 shows that the surface excess of CUPs increased with activity at dilute range. When the activity is higher than 1 mmol/L, the values of surface excess didn't follow the increasing trend. One possible reason is the invalidity of equation 4 and 5 in high concentration so that the activity values are not valid. Thus, the values of $\partial\gamma/\partial\ln(a)$ calculated from Figure 2 were not valid.

From Γ, the values of surface area occupied by a single particle, σ, were calculated by $\sigma = 1/\Gamma N_A$. The results were listed at Table 4. When comparing the values of σ with the largest cross-section area of CUPs, $S_{cross,}$ at each volume fraction, one will find that σ is smaller than S_{cross} in most cases (S_{cross} for CUP-1, CUP-2, CUP-3, CUP-4 are 907, 1385, 1661, 3317$\dot{A}^2$ respectively). The result is physically surprising since the polymer's glass transition temperatures are between 120-130 Celsius degrees, these polymers are hard solids at room temperature. Without coalescent agent, these particles should not be able to form a film. Thus, it is nearly impossible that the particles occupy less area than its area of cross-section. There is at least one possible reason that can explain this issue. If each CUP is almost completely immersed in the suspension, then the area occupied by each particle is only the cross-section at the water-N_2 interface as shown in Figure 4. This hypothesis was supported by the low N_2-water-solid contact angle of solid poly(methyl methacrylate-co-methacrylic acid). Park and his colleagues[18] reported the air-water-solid contact angle of poly(methyl methacrylate-co-methacrylic acid) with 10% methacrylic acid by weight is about 21°. When part of the acid groups were neutralized by base, the contact angle of the particle can be even lower[19]. Suppose that the contact angle, θ, is 10° for CUP-1 with highest concentration, then the radius of the circle will be $r = R_s \sin(10°) = 2.95\dot{A}$, which is comparable to 2.8$\dot{A}$ calculated from the value of σ.

Due to the presence of image charge[20], the repulsion energy between particles on the H_2O-N_2 interface is twice of that in suspension if the distance between particles is the same for both on the interface and the bulk. There is also the possibility of additional dipole-dipole interaction between the particles on the interface depending on the contact angle of particle in water[21]. Either case will cause two-dimensional colloidal crystal on the interface[22]. It will be interesting to investigate the surface structure by some radiation methods like small angle neutron scattering[23].

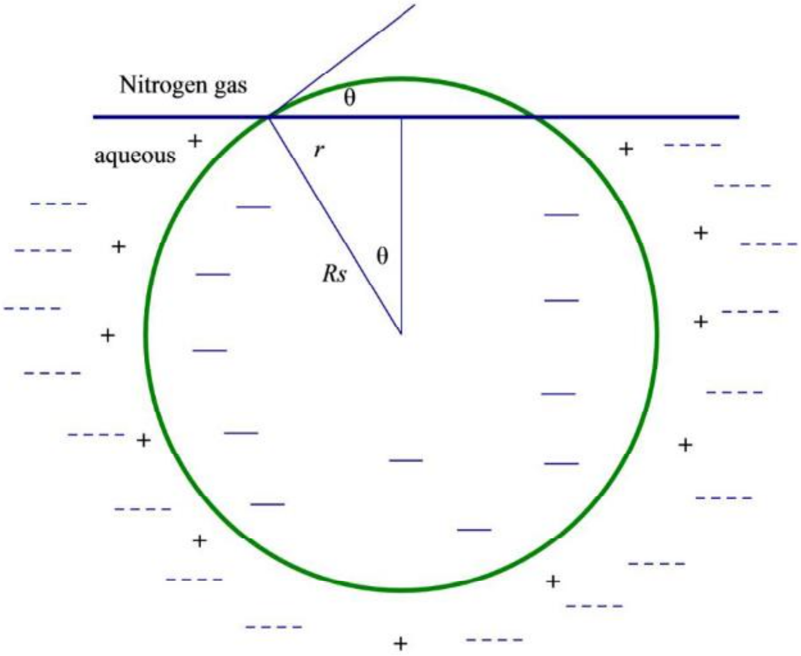


Figure 4. CUP particle immersed in water.

4. CONCLUSION

Surface tensions of CUPs of different molecular weights were evaluated at different concentrations. The results show that the surface activities of CUPs increase with molecular weight, which possibly results from the increasing hydrophobicity with increasing molecular weight. The surface excess of each CUPs increased with the activity of CUPs in when the activity was lower than 1mmol/m^3. The calculated area occupied by each particle was smaller than the largest cross-section area of CUP indicating that CUP particle barely sticks out of the liquid surface. Due to the interparticle repulsion and dipole-dipole interaction between the particles on the liquid-N_2 interface, the CUPs can form 2-D colloidal crystal on the water-N_2 interface. The further study on the structure of CUPs particle on the water-N_2 interface will be conducted.

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IV. RHEOLOGY STUDIES ON 3-7nm COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES IN PRESENCE OF NaCl

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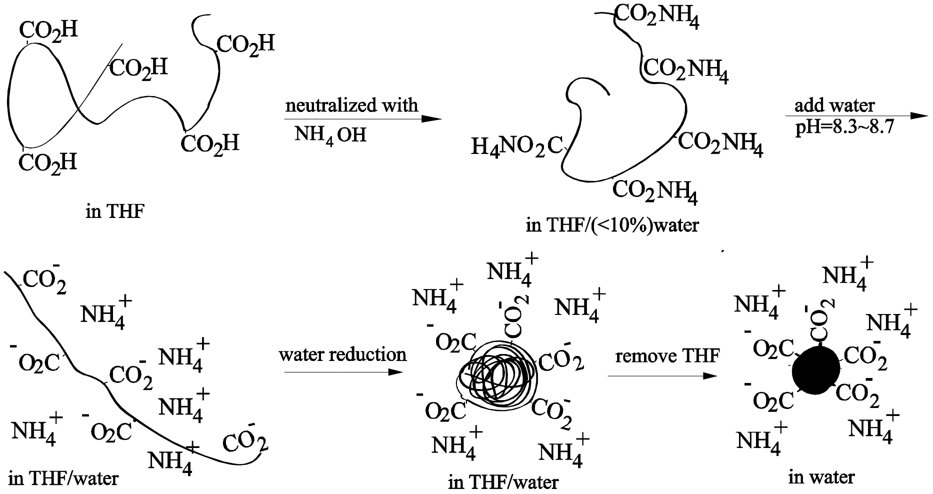
ABSTRACT

The rheological behaviors of CUPs were studied in presence of added electrolyte. When small amounts of external electrolytes were added, (<2% by weight), the viscosity of the suspensions (<0.06 by volume) dropped due to the screening effect of the added electrolytes. When the volume fraction of the suspension increased or the addition of electrolytes increased, the viscosities of suspension increased sharply at different critical points. Shearing viscosity of CUP suspensions showed the evolution of possible liquid structure with volume fraction and electrolyte concentration related to the radius of the particle with associated surface water and the salt with its coordinated water.

1. INTRODUCTION

The Colloidal unimolecular polymers (CUP) particles are formed from the collapsing of extended polyelectrolyte chain into globular structure in poor solvent like water. The formation of CUP particles is triggered by the polymer-polymer interaction being greater than the polymer-solvent interaction. Since release of the water molecules from the surface of polymer backbone into the bulk is an entropy increasing process, the transition undergoes spontaneously similar to the formation of micelle. [1] **Scheme 1** shows the process of formation of CUP particles. Once formed these colloidal particles are stable. Generally, the particle size of CUP particle is 3-9nm, which is similar to the size of common micelle, fullerene, and some proteins [2] .

Scheme 1. Process of formation CUP particles in water.



As described above, CUPs have negative charges on their surface, have a huge surface area per unit weight, and are stable in an alkaline aqueous environment. CUP particles are potentially a vehicle for drug delivery, coatings, and adhesives. One of the fundamental properties for the potential applications is the rheological behavior of the CUPs suspension in presence of electrolytes since many applications contain electrolytes (normal body fluid contain 0.9% of NaCl by weight).

As charge stabilized colloids, it is expected that the electroviscous effects, which include the primary, secondary and tertiary electroviscous effect[3], should play an important role on the rheological behavior of CUPs suspension. Among the electroviscous effects, the primary and secondary electroviscous effects are related with the surface charge densities, which will be affected by the ionic atmosphere around the charged particles. When the indifferent electrolytes are added to the suspension, the dissociated ions will screen the ionic repulsion between charged particles, and decrease the strength of repulsion. Hence, the viscosity should decrease. As more electrolytes are added, the associated water on sodium ion and chloride ions will have larger chance to associate with the surface water on the CUPs thus increase the viscosity of the suspension.

The possible salt effects on rheology should be reflected from the rheological behavior of suspensions under shearing. If added electrolytes screen the static electro-repulsion between charge particles, a charge-stabilized structure can break down and the suspension will become near Newtonian. On the other hand, if the suspension is structured, the suspension will turn out to be Non-Newtonian. The current work will test the hypothesis mentioned above, and develop a rheological model for behavior of CUPs for possible applications. The viscosity of solution as a function of volume fraction of CUPs and concentration of NaCl were investigated by capillary viscometer and cone-and-plate viscometer.

2. EXPERIMENTAL SECTIONS

2.1 Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. Methyl ethyl ketone and acetone was purified by drying with anhydrous magnesium sulfate followed by simply distillation. Tetrahydrofuran was dried and distilled same with methyl ethyl ketone, but under the protection of nitrogen or argon gas during distillation. MMA was removed of inhibitors by mixing with 10% sodium bicarbonate, and then rinsed twice with deionized water followed by rinsing with brine twice. MMA was then dried with magnesium sulfate, filtered, and distilled with presence of copper bromide and protection of nitrogen or argon gas. MAA was distilled with presence of copper bromide under vacuum. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Deionized water was used for all experiments.

2.2 Synthesis and Characterization of Poly(MMA/MAA) Copolymers. MMA and MAA were placed in a 500ml round bottom flask with a molar ratio of 9:1 in methyl ethyl ketone (MEK). The ratio of monomer to MEK is 1:2 by weight. The mixture was refluxed for 24 hours under argon with AIBN (0.073 mole % to monomers) as the initiator and 1-dodecanthiol as chain transfer agent. The un-reacted monomers and solvent were removed by roto vapor connected with vacuum pump. The product was dissolved in distilled acetone and precipitated in de-ionized water with mixing of high speed disperser. The wet polymer was placed in a 50°C oven to remove most of the water and then heated in vacuum to 50°C for 24 hours. The absolute molecular weight of the copolymers and distribution was measured using gel permeation chromatography by Viscotek model 305 manufactured by Malvern Corp. Flow rate of THF was 0.5ml/min, and the injection volume 100μl. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight.

2.3 Acid Number Measurement. Acid numbers (AN) were determined by the titration method found in ASTM D 974 modified by replacing hydrochloric acid with potassium hydrogen phthalate, and methyl orange with phenolphthalein. The dry polymers were dissolved in THF.

2.4 Density of Dry CUP. The dilute suspensions of CUP were dried in a vacuum oven heated at 50℃ in presence of solid sodium hydroxide to absorb carbon dioxide. The resulted solid was then heated at 110℃ to constant weights. The density of the dry CUP was measured by a gas displacement pycnometer: Micromeritics AccuPycII 1340. Volume of sample can be calculated as:

$$V_s = V_c + V_r/(1 - \frac{P_1}{P_2}) \tag{1}$$

where V_s is the sample volume, V_c is the volume of the empty sample chamber, V_r is the volume of the reference volume, P_1 is the first pressure (i.e. in the sample chamber only) and P_2 is the second (lower) pressure after expansion of the gas into the combined volumes of sample chamber and reference chamber. The temperature was maintained at 25.89±0.04℃ with presence of equilibrated helium flow at rate of 0.005psig/min. The results were reported by its average and standard deviation from twenty-five readings.

2.5 Water-reduction. Polymers were dissolved in tetrahydrofuran (THF) (10% w/w) and stirred overnight. Acid groups of the copolymer were neutralized by ammonium hydroxide according to its acid number. The equal amount of pH modified water (pH=8.5~9 adjusted by NH_4OH) to THF was added to the solution by a peristaltic pump at a rate of 1.24g/minute with the tip of tubing inside the solution. The pH of solution was maintained between 8.5 and 9. THF was then stripped in-vacuo. Solutions were then filtered through 0.45μm Millipore membrane to remove any foreign materials which were typically measured to be less than 0.05% by weight. The solution was diluted to different concentrations with pH modified water (pH was between 8.5 and 9). Higher concentrations were attained by stripping most of the water in-vacuo or evaporating water slowly in the presence of dry NaOH pellets in a deccicator. CUP suspensions with NaCl were prepared by mixing concentrated polymer solution with various concentrated NaCl solution to obtain desired concentration of polymer and NaCl.

2.6 Shearing Viscosities of CUP Solution. One milliliter of CUP solution was transferred by Eppendorf pipet to the sample well of cone-and-plate viscometer Brookfield LV DVIII manufactured by Brookfield. Constant temperature water bath at 25.0±0.1 ℃ were circulated through the sample well. Shearing viscosities of CUP suspension were measured under a series of increasing shear rates. The shear rates were programmed to increase at set speed and viscosities were recorded after continuously shearing for 1 minute at each speed. Only results with %Torque larger than 10% were counted as valid data.

2.7 Absolute Viscosity of CUP Solution. The suspensions were equilibrated in an Ubbelohde capillary viscometer (Cannon Inc.) immersed in a constant temperature water bath at 25.0±0.1℃ for 20 minutes before measuring with plastic wrap cover on top of the viscometer to prevent evaporation and CO_2 contamination. A stop watch with 0.01 second precision was used to monitor the elution time. The measurement was repeated at least three times. The estimated standard error was within 0.5%. Absolute viscosity was calculated by Eq. 2

$$\eta = t \cdot d \cdot c \tag{2}$$

where t, d, and c were elution time, density of solution and constants of Ubbelohde with unit second, g/ml and cP/second. The specific viscosity of solution was calculated as

$$\eta_{sp}=\eta/\eta_w \tag{3}$$

where η_w is viscosity of water with unit cP. Densities of solutions were measured with a pycnometer.

2.8 Particle Size of CUP and Distribution. Particle size and distribution were measured by dynamic light scattering instrument Microtrac Nanotrac 250 with viscosity of suspension instead of water as suggested by manufacture.

3. RESULTS AND DISCUSSION

3.1 Characterization of the Copolymer and CUP. The copolymer was dissolved in THF, neutralized with ammonia hydroxide. Deionized water with pH=8.5~9 modified by ammonia hydroxide was added followed by THF removal via reduced pressure distillation. The resulted CUP particles were suspended in water with pH=8.5~9. The particle size and density of CUPs along with the molecular weight and acid number of were listed in Table 1. From the acid number, the actual composition of copolymer can be calculated by Eq. 4.

$$\frac{nMMA}{mMAA} = \frac{\frac{56100}{AN} - Mw_{(MAA)}}{Mw_{(MMA)}} \tag{4}$$

If the density of CUP in suspension is assumed to be same as the density of dry polymer, then the theoretical equivalent spherical diameter of CUP can be estimated by $d = (\frac{6Mn}{\pi N_A \rho})^{1/3}$ where M_n is the number average molecular weight, N_A is Avogadro constant, ρ_p is the density of dry polymer. From the measured values of densities and acid number, the calculated diameter and composition for the CUP polymers are listed in Table 1.

Table 1. Molecular weight, density, diameter and acid number of CUPs.

Mn (kg/mol)	Mw (kg/mol)	Density (g/ml)	d_m[a]	d_c[b]	AN[c]	nMMA/mMAA
111	174	1.2342 ± 0.0018	6.5	6.6	62.2	8.2

a) measured particle size by DLS, nm; b) Calculated particle size from Mn, nm; c) Acid number, mgKOH/g polymer

3.2 Specific Viscosities of CUPs Suspension with and without NaCl Measured by Ubbelohde Viscometer. The specific viscosities of CUPs with different levels of NaCl were measured at various percent solids of CUPs. The results were presented in Figure 1. It shows that the addition of salt up to 4% lowers the viscosities of the suspensions except when the concentration of CUP exceed 12.5% solid. For suspensions with percent solids of CUPs lower than 7.5%, the viscosities were not sensitive to the addition of salt. When the percent solids of CUPs reach 10%, the viscosity became sensitive to higher concentration of salt. The CUPs are charged particles with negative carboxylic group on the surfaces. For charged particles in solution with electrolyte, charges will form electrical double layers on the surface of particles. When salt is added to the solution, the thickness of the electrical double layer is compressed due to the screening effect of the added sodium ions. Thus the effective surface charge of particle will decrease, and the additional increment of viscosity caused by surface charge will decrease.

As the salt concentration increased above 3%, the viscosity increased more significantly, especially for the 12.5% CUP solution. The possible reason is that significant amount of water molecules are associated on the surface of sodium and chloride ion, and are less mobile in the matrix of highly charged CUPs than bulk water. Suppose that the suspension with added electrolyte reach its random close packing when the total effective volume occupied by sodium, chloride ion, and CUPs is 0.634.[4] At this volume fraction, the suspension will gel up, i.e., the viscosity reach infinity. In the case of suspension with 12.5% of CUPs, the volume fraction, ϕ, is 0.1067 calculated from the weight fraction and density of the suspension by $\phi = \frac{f\rho_s}{\rho_p}$ where ρ_s is the measured density of suspension, 1.05g/ml, ρ_s is density of particle. Considering the surface water, the effective volume fraction is

$$\phi_{eff} = \phi(1 + \frac{\delta}{r})^3 = 0.1067 \times \left(1 + \frac{0.57}{3.25}\right)^3 = 0.17 \qquad (5)$$

where δ is the thickness of water layer, 0.57nm was calculated in previous research work. A recent simulation results shows that a sodium ion in aqueous solution is surrounded by two shells of water molecules, and the Na^+ to the oxygen atom of the water in the outer shell is $4.18\dot{A}$[5]. Mancinelli[6] reported the average center-to-center distance of Cl^- to the oxygen atom of water in the water layer is $3.16\dot{A}$. The effective volume occupied by each hydrated ion is 305.8 $\dot{A}^3$ for sodium ion and 153.2 $\dot{A}^3$ for chloride ion. In a 100g suspension with 12.5% CUP (w/w) and 4% NaCl (w/w), the density is 1.05g/cm^3, so the total volume is 95.2 cm^3. The total volume occupied by hydrated sodium and chloride ions can be calculated as

$$V_{NaCl} = \frac{4}{58.5} \times (305.8 + 153.2) \times 6.02 \times 10^{23} = 1.9 \times 10^{25} \mathring{A}^3 = 19\ cm^3$$

Thus, the total volume fraction of hydrated sodium and chloride ion is 19/95.2=0.20. The total volume fraction of CUP and hydrated sodium and chloride ions is 0.17+0.20=0.37. The relative viscosity of the suspension can be estimated by Quemada equation[7]

$$\eta_r = (1 - \frac{\phi}{\phi_{max}})^{-2} \tag{6}$$

where ϕ is solid volume fraction, ϕ_{max} is maximum random close packing volume fraction, 0.634. The resulted η_r was found to be 5.8. That is, the specific viscosity is 4.8, which is close to the measured value 4.4. Therefore, it can be concluded that the CUP and hydrated electrolyte ions contribute to the viscosity augment of the suspension with 4% salt.

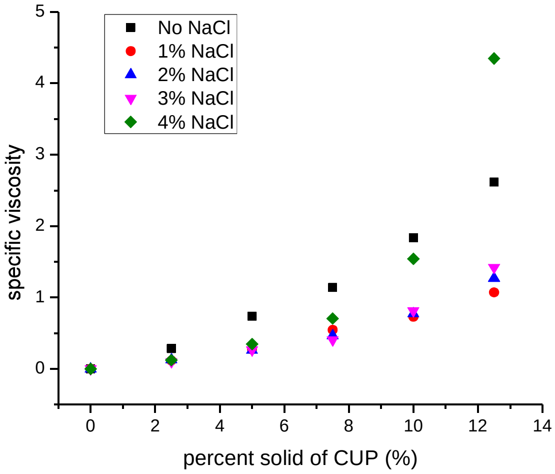


Figure 1. Specific viscosity of CUPs versus concentration at different levels of NaCl.

3.3 Shearing Viscosities of CUPs Suspension with and without NaCl Measured by Cone-And-Plate Viscometer. In order to investigate the possible effect of salt addition and percent solid of CUPs on the rheological behavior of CUP suspensions, the shearing viscosities, $\eta_{s,}$ and shear stresses, σ, were monitored under increasing shearing rate, $\dot{\gamma}$. The results were presented in Figure 2 and Figure 3. The apparent trend in Figure 2 was that the shearing viscosities of the suspension with 2.5% CUP was insensitive to addition of salt. For those suspensions with higher percent solid (5%-12.5%), the shearing viscosity was dependent on shear rate and the addition of salt. The suspension with 12.5% CUP and 4% NaCl gelled 24 hours after preparation probably because of floc formation. As the large amount of added electrolyte ions (compared with number of CUP particles) condensed on the surface of CUP particles,[8] suppressing the dissociation of counterion from the carboxylic groups of CUP particle, the electrical double layer of CUP was highly compressed. According to classical DLVO theory[9, 10], the electro-repulsion energy between the CUPs decreased so that the attractive force resulting from Van der Waals force overcame the repulsive force, and the CUPs tend to approach each other. In addition, the CUP particle tended to aggregate to minimize the surface energy since the specific area of CUP is very large due to its small particle size.[11] The process of aggregating is time-evolving.[12] That's why the fresh-made suspension didn't gel immediately and could still flow through the capillary viscometer. The aggregate of CUP is very open in structure and can be broken by shear. In term of rheology, the suspension will show shear thinning. In order to quantitatively analyze the rheological behavior of CUP suspensions with salt, Casson's[13] model and power law[14] model were used to fit the relationship between shear stress and shear rate.

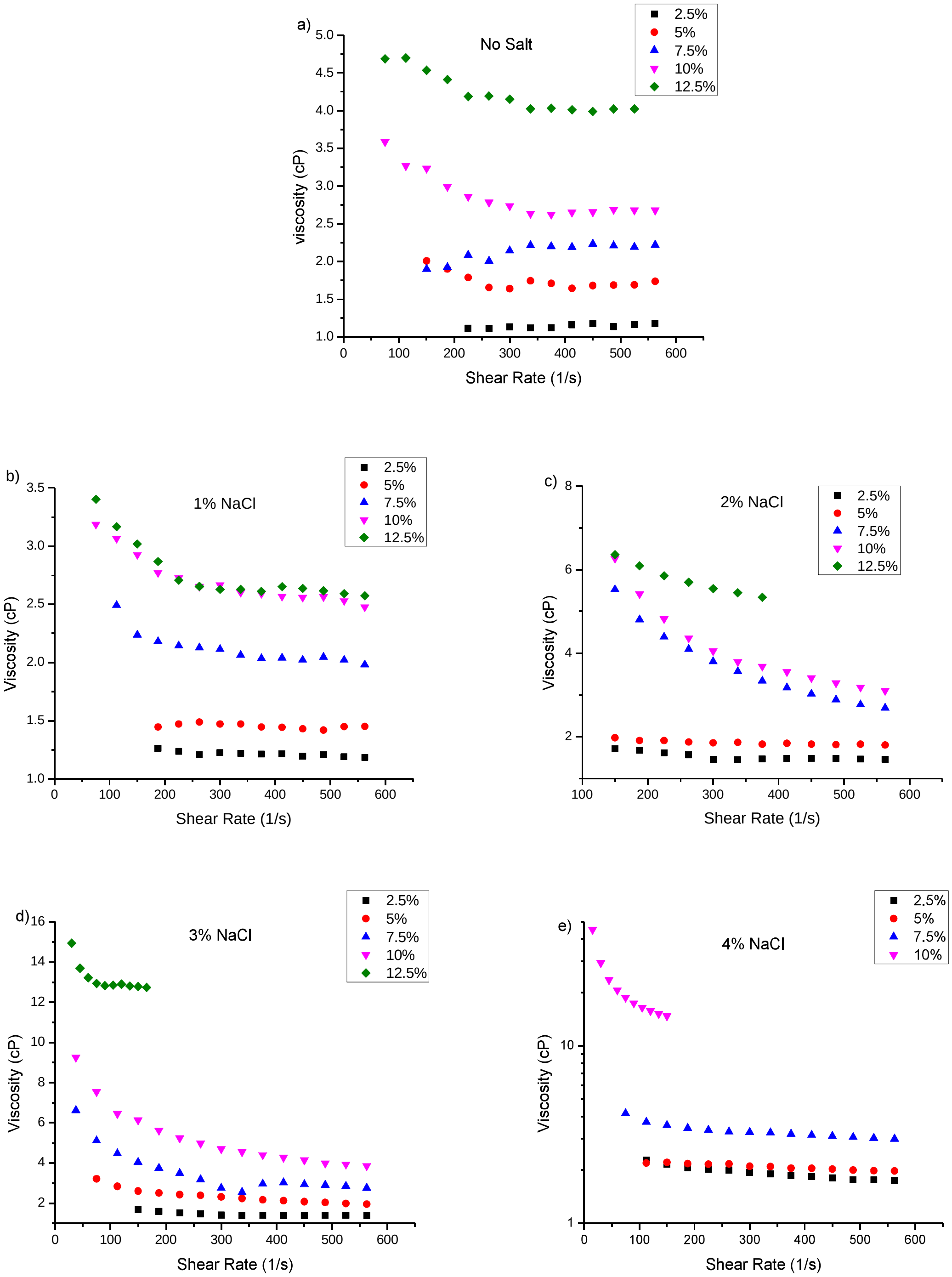


Figure 2. Shearing viscosities of CUPs with different percent solids at various NaCl addition. a) without salt; b) 1% NaCl; c) 2% NaCl; d) 3% NaCl; e) 4% NaCl. The suspension with 12.5% CUP and 4% NaCl gelled, and the viscosity couldn't be measured by the current rheometer.

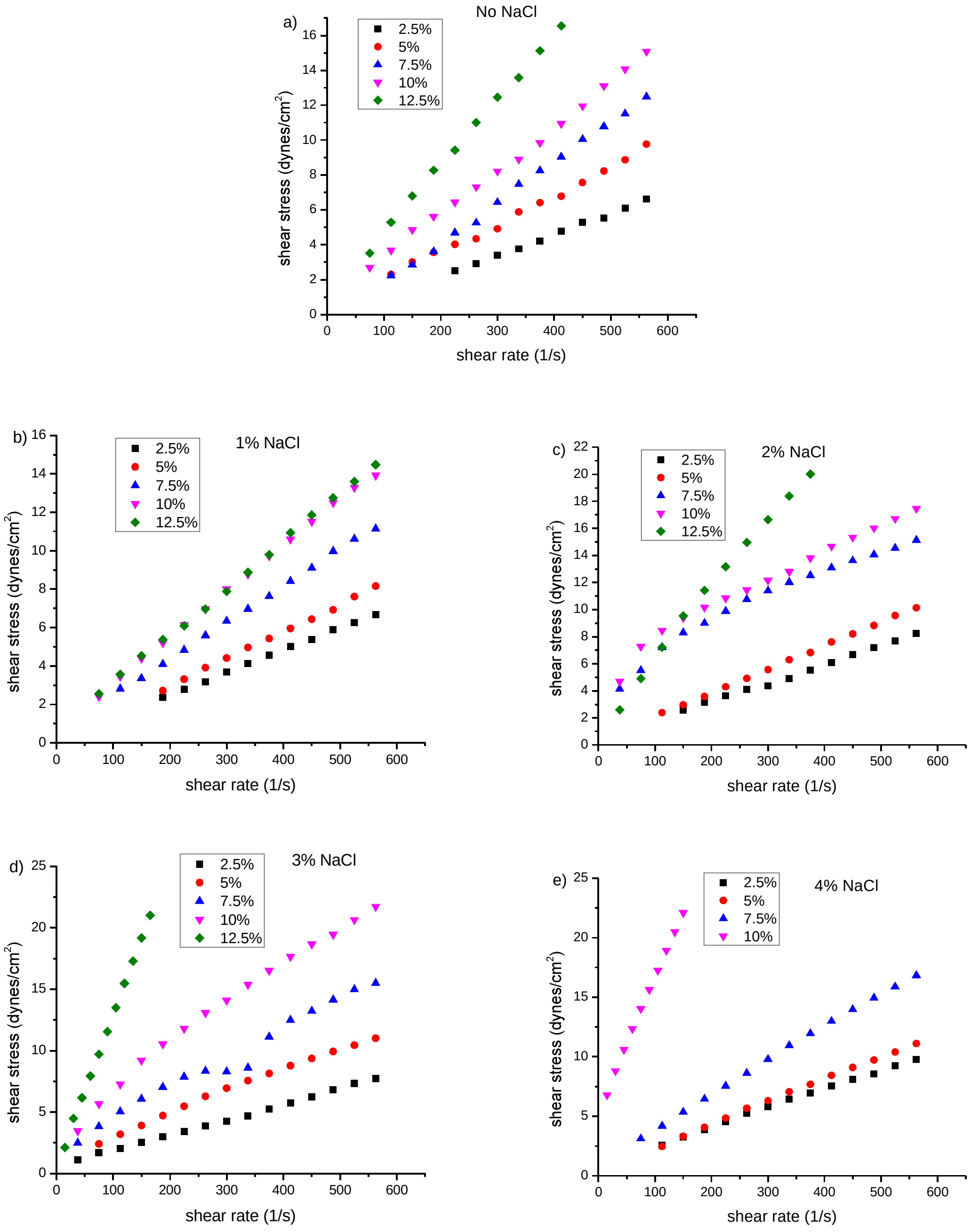


Figure 3. Shearing stresses of CUPs with different percent solids at various NaCl addition. a) without salt; b) 1% NaCl; c) 2% NaCl; d) 3% NaCl; e) 4% NaCl. The suspension with 12.5% CUP and 4% NaCl gelled, and the shear stress couldn't be measured by the current rheometer. The possible reason refers to the text.

Casson equation can be expressed as equation 7 where σ is the shear stress, σ_0 is the yield stress, η is the plastic viscosity, and $\dot{\gamma}$ is the shear rate. The closer the value of σ_0 is to zero, the more likely the suspension behaves as a Newtonian fluid.

$$\sqrt{\sigma} = \sqrt{\sigma_0} + \sqrt{\eta\dot{\gamma}} \qquad (7)$$

The power law model is presented as equation 8 where k is consistency, $\dot{\gamma}$ is the shear rate, and n is power index. With $n < 1$, a shear thinning fluid is described, while $n > 1$ describes shear thickening. If $n = 1$, the fluid is Newtonian. The data in figure 3 was fit with equation 5 and 6, and the fit values of σ_0 from equation 5 and n from equation 8 were presented in Figures 4 and 5.

$$\sigma = k\dot{\gamma}^n \qquad (8)$$

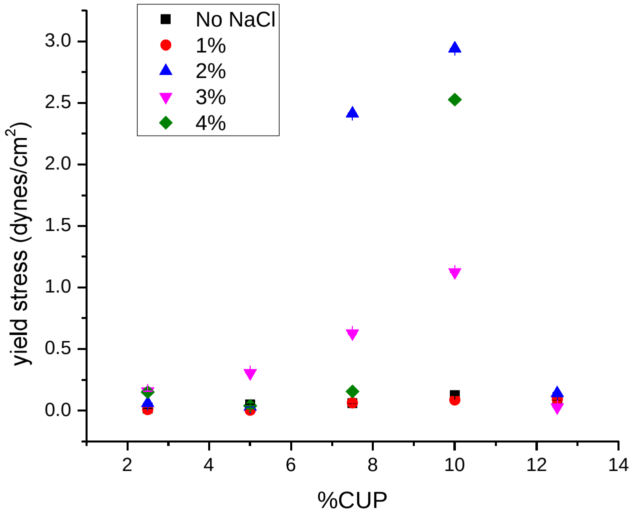


Figure 4. Yield stresses as a function of %CUP and added NaCl.

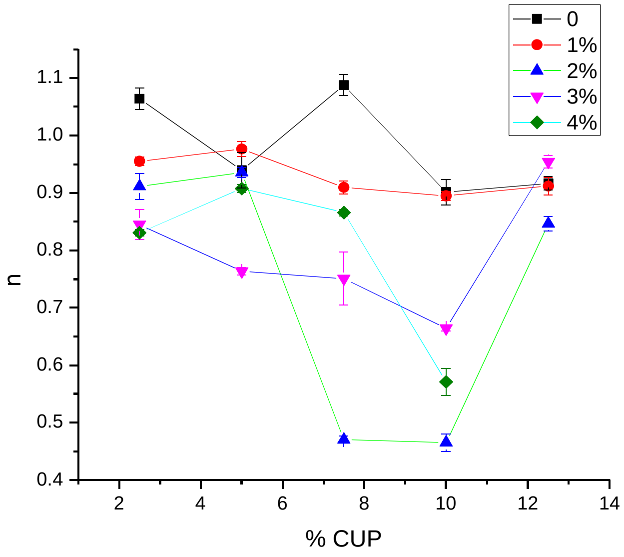


Figure 5. Power indices as a function of %CUP and added NaCl. (connected line is only to lead eyes).

Figure 4 shows that when the addition of salt was fixed there exists a maximum yield stress as percent solid of CUP increase, which is more significant for suspension with higher level of added NaCl. The trend was similar in Figure 5 where there exist a minimum in *n* as the percent solids of CUP increases. It indicates that there might exist a combination of percent solid of CUP and salt addition where the suspension was most pseudo-plastic. Without added electrolytes, the charge repulsion between particles keeps the particle from each other, and makes the suspension structured. When the percent solid of CUP was low, small amounts of additional electrolyte screen the charge repulsion between the charge particles, decreasing the stability of the structure. Therefore, the suspension behaved close to Newtonian fluids. It can be reflected from the *n* values of suspension which are close to 1 for suspensions of 2.5% and 5% in Figure 5. As more electrolytes were added, the associated water on the sodium ion and chloride ions play more important roles compared with the screening effects. As shown in the calculation in

Section 3.2, the associated water on the sodium and chloride ion of 4% of added NaCl account for 19% of total volume. The associate water can form hydrogen bond with the surface water of CUPs. Also the sodium ions on the surface of CUPs can share associated water with the sodium ion in the bulk suspension. In addition, due to the decreasing of electro-repulsion, the CUP particles tend to aggregate. All the factors mention above contribute to the augmentation of the structure of suspension, therefore the viscosity increase significantly. The shear thinning behavior is not significant since the applied shear rate was not high enough to break down the structure.

4. CONCLUSIONS

Viscosities of CUPs suspension with various percent solids and addition of NaCl were measured by capillary and cone-and-plate viscometer. Results from both sources indicate that there exists a synergistic effect between percent solid of CUPs and added electrolyte on rheological behavior of CUPs suspension. This discovery is of great importance to the possible application of CUPs in presence of electrolyte as drug delivery systems since the high viscosity needs to be avoided. In the future, more research will be focused on rheological behavior of the polymer solution in the presence of other monovalent electrolytes like LiCl and KCl and multi-valent electrolyte like Na_2SO_4.

5. ACKNOWLEDGEMENTS

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V. MOLECULAR WEIGHT (M_n) AND FUNCTIONALITY EFFECTS ON CUP FORMATION AND STABILITY

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(Submitted for publication as an Article in the *Journal of Coatings Technology: Research*)

ABSTRACT

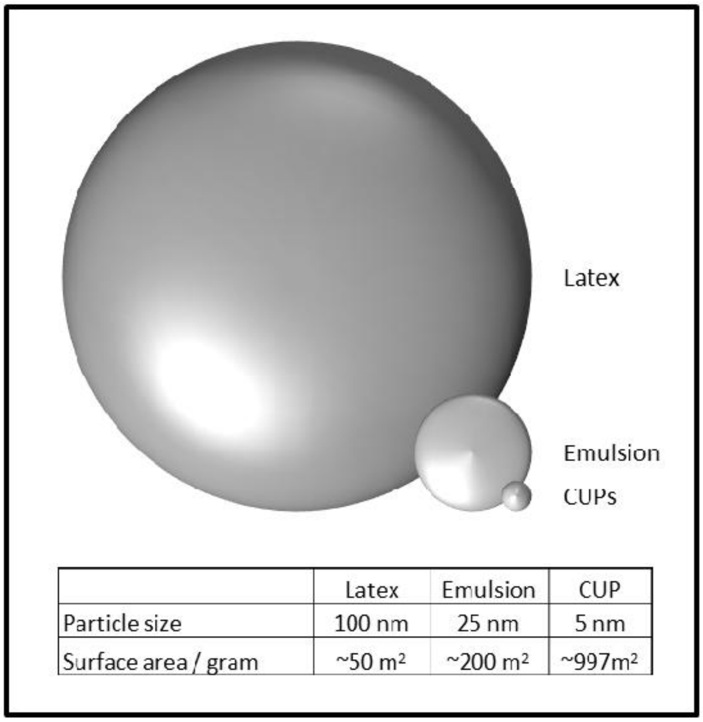
The formation of colloidal unimolecular polymer, CUP, particles from single polymer strands was investigated as a function of molecular weight. The CUP particle size was correlated with the absolute molecular weight and its distribution. The characteristics of the particles were evaluated with respect to viscosity, acid number, size distribution and stability. The particle size varied from less than three nanometers to above eight nanometers representing polymers with molecular weight in the range of 3,000 to 153,000. Lower molecular weight polymers were found to be unstable. Particle size measurements using Dynamic Light Scattering technique indicated a normal distribution which corresponded to the molecular weight distribution of the copolymer. The statistical distribution of the acid groups in the polymer chains played a significant role in the stability of low molecular weight polymers.

Keywords: Colloidal unimolecular polymer (CUP), Molecular weight, Stability, Particle size distribution, Aggregation

1. INTRODUCTION

Micelle formation of amphiphilic polymers has been a topic of huge interest lately because of its diverse applications ranging from an understanding of protein folding and drug delivery to its application in polymers and coatings in general. Kabanov A, et.al. studied micelle formation of block copolymer based on hydrophilic poly(ethylene oxide) and hydrophobic poly(propylene oxide).[1] Kataoka K, et al., demonstrated micelle formation of diblock copolymers of poly(aspartic acid) as the hydrophobic block and poly(ethylene glycol) as the hydrophilic block.[2] These copolymers and similar other amphiphilic diblock copolymers which form polymeric micelles suffer from a major drawback in the sense that they are dynamic entities and demonstrate micelle-like properties only above a critical micelle concentration (CMC). As a solution to this problem, Uhrich K, et. al. synthesized hyperbranched polymers with a hydrophobic core and a hydrophilic shell, which, because of its covalently bound structure gives stable micelle-like structures.[3-5] Moroshima et al. studied micelle formation through intramolecular aggregation of random copolymers of 2-acrylamido-2-methylpropanesulfonate (AMPS) and methacrylamides N-substituted with bulky hydrophobic groups with cyclic structures like cyclodecyl, admantyl and 1-naphthyl.[6-8] In both the cases, the polymers studied are readily soluble in water which hampers its application in paints and coatings and also the particle size of these polymeric micelle are not in the true nano-scale region (<10 nm).

Recently, the authors have reported the synthesis of a new type of micelle-like, true nano-scale materials which were termed as colloidal unimolecular polymer particles (CUPs). Some of the interesting features of CUPS include zero volatile organic content (VOC), particle size in the range of 3–9 nm and an easy and efficient synthetic procedure. CUPs are solid unimolecular polymer particles suspended in an aqueous phase. Figure 1 illustrates the size comparison of a conventional latex particle, waterborne urethane resin and Colloidal Unimolecular Polymer (CUPs) particle[9].



	Latex	Emulsion	CUP
Particle size	100 nm	25 nm	5 nm
Surface area / gram	~50 m^2	~200 m^2	~997m^2

Figure 1. Comparison of size of latex, emulsion and CUP particle.

CUPs are typically prepared from polymers containing hydrophilic groups such as carboxylic acid salts or sulfonate acid salts on the hydrophobic polymer backbone. The amount of hydrophobic and hydrophilic groups on the polymer chain (HLB value) play a critical role in the unimolecular collapse of the random acrylic polymer chains during the process of water reduction. The collapse of polymer chains in the aqueous solution is favored by a higher polymer-polymer interaction as compared to polymer-solvent interaction and entropically favored by the release of water which is associated with the surface of polymer chains. The polymer chains which are in a state of random coils in THF undergo a conformational change as the solvent environment around the polymer is changed by way of neutralization with a base and addition of water. The random coil conformation in THF transits to an extended chain conformation with neutralization of acid groups and water addition because of the ionic repulsion along the polymer chain and then finally to a collapsed globule like conformation. When the concentration of polymer in the solution is dilute the polymer chains collapse unimolecularly and these CUPs are then stabilized by the carboxylate groups through electrostatic repulsion.[10]

In this paper, we explore the effect that the molecular weight of the acrylic copolymers has on the formation and stability of colloidal unimolecular polymer particles. We synthesized nine random copolymers of methyl methacrylate and methacrylic acid with a molecular weight in the range of 3000 to 153000 and investigated their ability to water-reduce to form colloidal unimolecular polymer particles with a stable particle size in the true nano-scale region (<9 nm).

2. EXPERIMENTAL

2.1 Materials. Methacrylic acid (MAA), methyl methacrylate (MMA), 2,2′-azobis (2-methylpropionitrile) (AIBN) and 1-dodecanethiol were purchased from Aldrich. Inhibitors from MMA were removed by washing with 10% aqueous solution of sodium bicarbonate ($NaHCO_3$), brine solution and distilled water respectively and further purified by distillation. MAA was purified by distillation with copper (I) bromide under vacuum. AIBN was re-crystallized from methanol prior to use and n-butanethiol was used as received. Tetrahydrofuran (THF) was purchased from J. T. Baker and purified by distillation before use.

2.2 Polymer Synthesis. Copolymers of MMA and MAA were prepared in a 3-neck flask equipped with a thermometer, a nitrogen inlet and a condenser fitted with a mineral oil isolation positive pressure bubbler. MMA and MAA monomers were charged into the flask in a molar ratio of 9:1 along with the solvent THF and n-butanethiol as a chain transfer agent. AIBN was used as the free radical initiator and the polymerization reaction was carried out under refluxing conditions for 24 hrs. The polymer solution was then cooled to room temperature and precipitated in cold de-ionized water under high shear and then filtered. For further purification, the polymer was re-dissolved in distilled THF and precipitated in cold water under high shear, primarily done to get rid of most of the unreacted MAA monomer as it is water-soluble. The traces of un-reacted MMA and THF were removed by placing the polymer in a desiccator under high vacuum. The polymers were thoroughly dried using a freeze-drier. Polymers with different molecular weights were synthesized by controlling the amount of chain transfer agent n-butanethiol. The formulation for the polymers synthesized is listed in Table 1.

2.3 Synthesis for 12K Polymer. The monomers, MMA (0.9 moles, 91.3 g), and MAA (0.1 moles, 8.7 g) and the solvent (THF) were charged in a 500 ml 3-necked round bottom flask fitted with a nitrogen inlet, a mechanical stirrer, a thermometer, and a reflux condenser with a gas bubbler tower at the top to allow a positive flow of nitrogen throughout the polymerization. Then the chain transfer agent initiator i.e. n-butanethiol (0.008 moles, 0.75 g) was added to the reaction mixture. While stirring the reaction mixture, the 3-necked flask was purged with nitrogen gas for about 15 minutes to get rid of oxygen before adding the initiator. After purging, the freshly recrystallized free radical initiator i.e. AIBN (0.0007 moles, 0.12 g) was added. The flask was heated slowly to reflux and allowed to react for 24 hours. The polymer solution was then cooled to room temperature and the polymer was precipitated in cold de-ionized water under high shear. Then the polymers were dried completely using a freeze drier. All the polymers were synthesized according to the protocol.

2.4 Characterization of Polymers Synthesized. Absolute number average molecular weights (Mn) were measured by gel permeation chromatography (GPC) on a Viscotek GPCmax from Malvern instruments coupled with a triple detector array TDA305 (static light scattering, differential refractometer and intrinsic viscosity). Acid value (AV - reported in mg of KOH/ g of polymer sample) for all polymers were measured by titration method mentioned in ASTM D-974 which was modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, and phenolphthalein as an indicator in place of methyl orange.

Table 1. Formulation for MMA-MAA polymers.

Polymer	Acrylate: acid molar ratio	Monomer:Thiol ratio
Poly-1	9:1	28:1
Poly-2	9:1	55:1
Poly-3	9:1	106:1
Poly-4	9:1	155:1
Poly-5	9:1	201:1
Poly-6	9:1	246:1
Poly-7	9:1	824 :1
Poly-8	9:1	1030 :1
Poly-9	9:1	1648 :1

2.5 Water-reduction of MMA-MAA Based Copolymers to Form CUPs. The purified and dry acrylic copolymers were dissolved in dry and distilled THF; a low boiling and water miscible solvent. The polymer was stirred overnight for complete dissolution of polymer chains. Aqueous ammonium hydroxide solution (28% w/w) was added to neutralize all the acid groups on the copolymer based on the acid number of the copolymer. Deionized water modified to a pH of 8~9 using 28% aqueous NH_4OH solution was then added to the polymer solution by a peristaltic pump at a rate of about 1.24g/minute. The pH of solution was maintained at 8-9 throughout the process of water reduction. THF was then stripped off under vacuum to give CUPs in VOC free aqueous solution. The CUP solutions were then filtered through 0.45μm Millipore membrane to remove any impurities. Water reduction process-Poly-4 (MW=12K): 10 g of poly (MMA-co-MAA) was dissolved in 40g of THF to make a 20% w/w solution. The carboxylic- acid groups were neutralized by adding 28% aqueous NH_4OH solution and

90g of deionized water was then added by means of a peristaltic pump. The THF was then completely stripped off in-vacuum. Then the sample was concentrated by stripping off water to give a 20% w/w CUP solution of poly (MMA-co-MAA) in water. Figure 2 shows the process of formation of CUP particles with carboxylate groups on their surface, preventing the particles from aggregating through electrostatic repulsion.

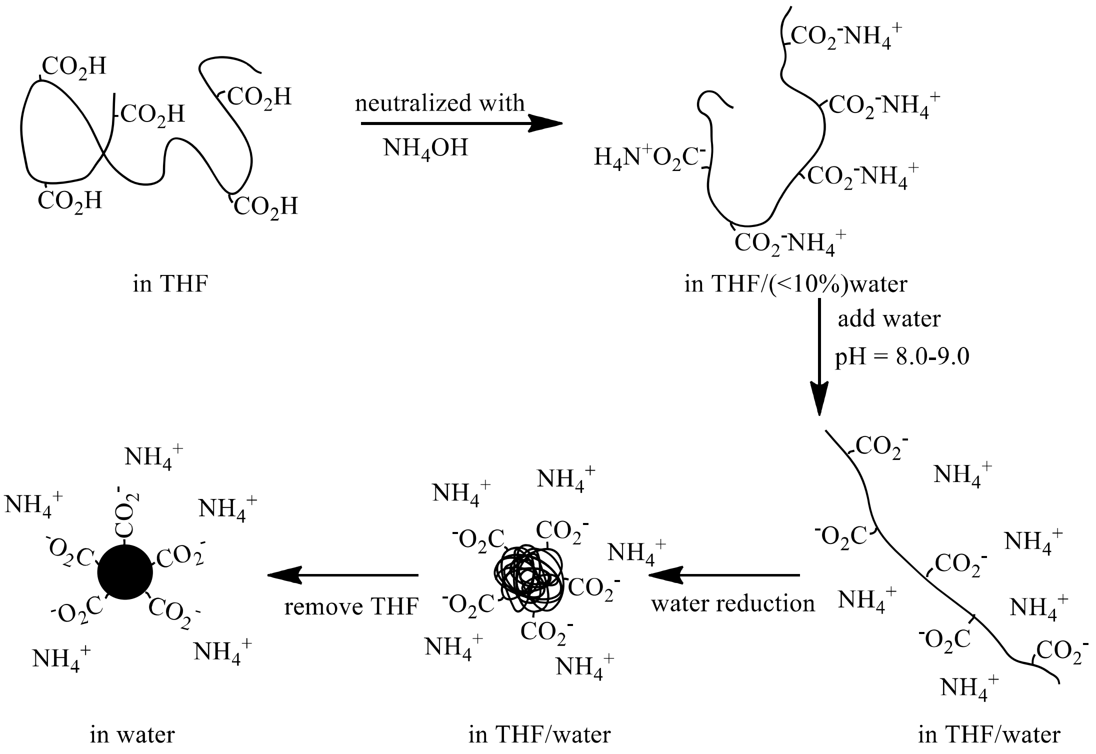


Figure 2. General process of formation of CUPs.

The water reduction process for CUP particle is depicted above in Figure 2. The polymer had a hydrophobic backbone of methyl methacrylate and a hydrophilic methacrylic acid side-chain in a molar ratio of 9:1. When dissolved in THF (dielectric constant = 7.58 at 25°C) the polymer chain was a random coil based upon the Mark-

Houwink exponent 'a'. The value of the Mark-Houwink constant 'a' for polymers above 15K was 0.66 ± 0.03 but for low molecular weight polymers the value obtained was not reliable. When base i.e. ammonium hydroxide was added to the solution, the carboxylic acid groups on polymer chain formed ion pairs of COO^- and NH_4^+. When pH modified water (pH = 8-9) was added using peristaltic pump, the formed ion pairs become solvated and separate. Negatively charged carboxylate groups then repelled each other due to the increasing dielectric caused by the added water (dielectric constant = 78.39 at 25°C)[11] and the polymer chain stretched causing an increase in the viscosity. With continuous addition of water, at a critical point in the composition, these amphiphilic polymer chains collapse. The carboxylate groups being hydrophilic orient into the water phase, organizing to produce maximum separation of charge and the stretched hydrophobic polymer chain collapsed to form spheroidal CUP particle. The unimolecular collapse was also dependent on molecular weight and on concentration of this amphiphilic polymer in THF and THF/water mixture, because, at higher concentration polymer chains overlap and if overlapped polymer chains come in contact with each other at critical point, non-unimolecular collapse occurs forming bigger particle size or coagulum. When carboxylic acid groups are used, the water must be free of polyvalent cations like calcium which cause aggregation and gelling.

2.6 Characterization of CUPs. After the water-reduction process which includes the removal of THF, viscosity measurements of CUP solutions were done using the Brookfield LV DVIII rheometer for use in particle size measurements. Viscosities at two different temperatures were measured, one at 25^0 C and other at 29^0 C. Shearing viscosities of CUP at different shear rate were measured. The shear rates were programmed to increase at set speed and viscosities were recorded after continuous shearing for 1 minute at each speed. Particle size and distribution were measured by dynamic light scattering on a Nanotrac 250 particle size analyzer from Microtrac with a laser diode of 780 nm wavelength, and 180° measuring angle.

3. RESULTS AND DISCUSSION

3.1 Acid Number. The experimental value of acid number was slightly greater than the theoretical acid number which can be explained by the loss of some of the MMA monomer which was more volatile of the two monomers, through evaporation with solvent during the polymerization. In Table 2 are listed the values for acid number and percent yield for the polymer synthesized.

Table 2. Percent yield and acid value of polymers.

Polymer Synthesized	Percent Yield (%)	Acid Value	
		Theoretical	Experimental
Poly-1	80	56.8	57.7
Poly-2	89	56.8	57.1
Poly-3	85	56.8	58.4
Poly-4	84	56.8	58.2
Poly-5	90	56.8	57.3
Poly-6	80	56.8	57.3
Poly-7	75	56.8	57.8
Poly-8	78	56.8	57.1
Poly-9	76	56.8	58.4

3.2 Molecular Weight Determination. Molecular weight and the polydispersity index for all the polymers synthesized are listed in Table 3. The number average molecular weight (M_n) as determined by the GPC was close to the targeted molecular weight for all the polymer samples.

Table 3. Molecular weight, polydispersity index and number of acid groups per polymer chain of the synthesized polymers.

polymer ID	Mn[b]	PDI[c]	N[d]
Poly-1	3.5[a]	1.2	3.5
Poly-2	4.5	2.02	5
Poly-3	8.5	1.79	9
Poly-4	13	1.48	13
Poly-5	15	1.6	15
Poly-6	20	1.32	21
Poly-7	72	1.19	74
Poly-8	90	1.15	92
Poly-9	153	1.27	157

a) 4mg/cc in THF. All other polymers were run at 2 mg/cc in THF; b)Number average molecular weight, with unit kg/mol; c) Polydispersity index; d- Number of acids group per polymer chain

3.3 Water-reduction of the Polymers to Prepare CUPs. All the polymers except the Poly-1 sample (MW = 3.5K) undergo water-reduction to give a clear, transparent CUP solution without any visible aggregate formation. The poly-1 sample however precipitated out during the solvent (THF) removal step to give a white, turbid solution with solid polymer particles. The molar ratio of MMA: MAA in the polymer was 9:1 which means that on an average, three carboxylic acid groups are present on an individual polymer chain of the Poly-1 sample. Simha and Branson first gave a general description of sequence distribution and chemical composition distribution in random copolymers[12] which was later simplified by Stockmayer[13]. According to Stockmayer, for free radical random copolymerization, the composition of the copolymer at any instant depends upon the concentration of growing free radical chains which is a function of the reactivity ratios of monomers, monomer concentration and number average degree of polymerization. The concentration of growing radical can be expressed as a power series of composition deviation which leads to a Gaussian distribution of chain composition about the mean value. As a result, for the MMA-MAA copolymer synthesized, the acid groups on the polymer chains has a normal distribution similar to the molecular weight distribution (polydispersity). These carboxylic acid groups after being neutralized to carboxylate groups provide the necessary stability to CUP particles through electrostatic repulsion. The formation of solid polymer particles during the solvent removal step for Poly-1 sample indicated that there is not sufficient stabilization from the electrostatic repulsion arising from the three carboxylate groups for a unimolecular collapse of individual chains. This leads to aggregation of polymer chains which results in some polymer precipitating out of the solution. We evaluated the acid value of precipitated polymer to verify that the precipitated polymer had lower number of acid groups. The solid polymer particles were first filtered from the CUP solution and then dried to constant weight in vacuum. The acid value of the precipitated polymer (Poly-1) was 28.4 mg KOH/ g of polymer which was about half of the acid value of the synthesized polymer (Poly-1). This clearly indicated that the polymer chains with low number of acid groups had precipitated out because of insufficient stabilization. The remaining CUP solution was then filtered through a 0.45 micron filter and analyzed further for viscosity and particle size measurement. A comparison of the turbid CUP solution of poly-1 before filtering, the clear CUP solution of poly-1 after filtering and the clear CUP solution of poly-5 (MW = 16K) is shown in Figure 3.

The concentration of polymer in THF can affect the unimolecular collapse of the polymer chains during water reduction. Dilute concentration prevents the polymers from aggregating during water-reduction. So, polymers up to Mn = 20K were dissolved in THF at a concentration of 20% weight solids, Poly-7 (72K) and Poly-8 (90K) at 10% weight solids and Poly-9 (153K) was at 5% weight by solids to avoid overlap of polymer chains during water reduction process. High molecular weight polymeric chains begin to overlap when the distance between them becomes on the order of their hydrodynamic size in solution and if this occurs then collapse will not be unimolecular.

Figure 3. Vial 1: CUP solution of poly-1 before filtering; Vial 2: CUP solution of poly-1 after filtering; Vial 3: CUP solution of poly-5 (MW = 16K).

3.4 Viscosity Measurements of CUP Solutions. The viscosity values for all the CUP solutions are listed Table 4. The viscosity of CUP solutions increased with increasing molecular weight of polymers. For each CUP solution, at both 25^0 C and 29^0 C, the shear stress on CUP solution increased linearly with increasing shear rate which indicates that the CUP solutions behave as a Newtonian fluid at these concentration. But at higher concentrations (above 15% wt/wt solids) they begin to show shear-thinning behavior. The increase in viscosity with molecular weight was not anticipated. However, it can be easily explained by the increased charge density on the surface of CUP particle with increased molecular weight of the polymer. A representative plot of shear stress against the shear rate for samples Poly-4, Poly-7 and Poly-8 is shown in Figure 4, Figure 5 and Figure 6 respectively.

Table 4. Percent solids and viscosity at 25℃ and 29℃ for CUP particles.

Polymer ID	% Solids	Viscosity (cP)at 25℃	Viscosity (cP) at 29℃
Poly-1	12.53	4.51	4.30
Poly-2	18.86	6.79	5.16
Poly-3	19.93	8.25	7.47
Poly-4	19.47	8.96	8.06
Poly-5	22.05	10.00	8.84
Poly-6	19.88	14.10	9.26
Poly-7	9.07	3.96	2.43
Poly-8	8.88	4.30	2.73
Poly-9	4.82	1.55	1.45

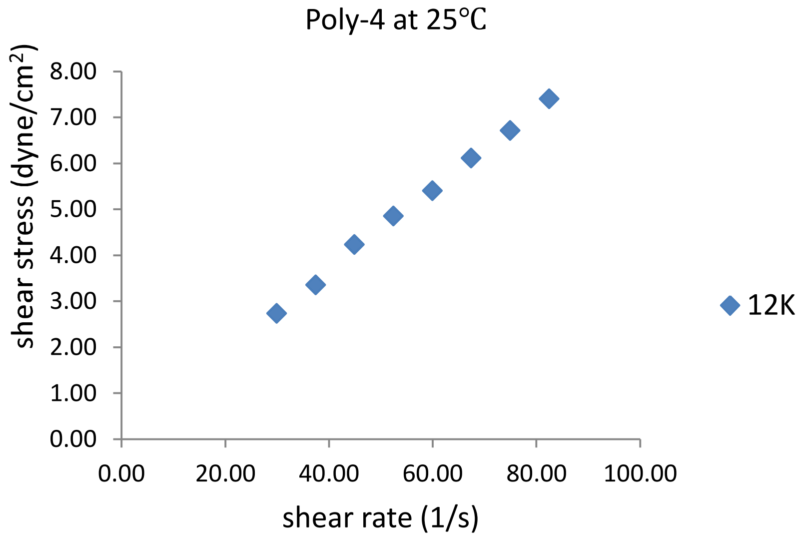


Figure 4. Shear stress against shear rate for Poly-4 at 25℃.

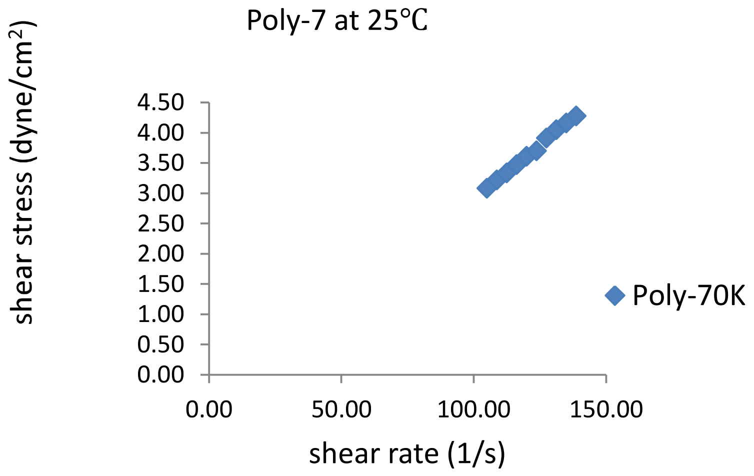


Figure 5. Shear stress against Shear rate for Poly-7 at 25℃.

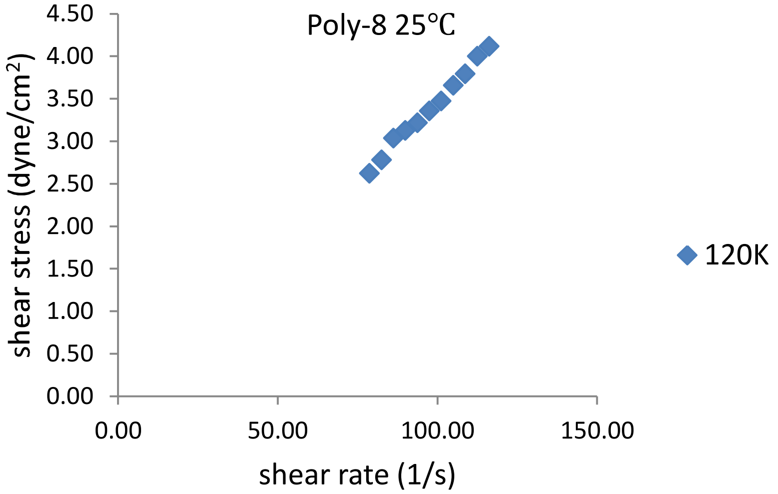


Figure 6. Shear stress against shear rate for Poly-8 at 25℃.

For acrylic latexes the viscosity is independent of molecular weight of the resin and depends primarily on the particle size.[14] For water-reducible resins, the application viscosity is independent of molecular weight in the dilute regime where there is no long range charge interaction and depends only on the particle size as governed by Einstein's theory of viscosity of dispersions of non-charged particles.[15,16] But as the concentration crosses into the semi-dilute regime, the viscosity builds up due to charge interaction and could be explained by fitting various viscosity models, one of them being the Ruiz-Reina's model.[17] But in the case of CUPs, the viscosity depends on both the molecular weight and particle size. The viscosity of CUP solution increases with increasing molecular weight of the copolymer. For all the three types of resins, the viscosity of the solution increases with decreasing particle size. Lower the particle size, higher the surface area which leads to higher amount of bound surface water and apparent increase in viscosity.[18,19] Since latexes usually have a particle size of about 100nm, the viscosity is quite low even at high solids and hence we can go to a maximum of about 65% resin solids while formulating a paint.[20,21] Water-reducible resins on the other hand have smaller particle size in the range of about 25nm which leads to a lower maximum percent resin solids of about 45-50%. In comparison, the CUPs have the lowest particle size of all the three and hence the maximum possible resin solids is about 30% after which it gels. But, CUPs offer significant advantage in terms of its volatile organic content (VOC). In case of the water reducible resins, the amount of solvent required to dilute the resin increases with increasing molecular weight of the resin. So, high VOC for high molecular weight water reducible resins.[22,23] But in our case, all the organic solvent is removed during the CUP formation process irrespective of the molecular weight of the polymer.

3.5 Particle Size Analysis. To show that the CUP particles were unimolecular, information from two techniques was compared. The absolute molecular weight (Mn) from GPC was used to calculate a theoretical diameter of collapse polymer chain and dynamic light scattering (DLS) was used to measure the experimental particle size of the CUP particles. Table 5 shows the comparison of the theoretical and experimental particle size of CUPs. There was good agreement between the experimental particle size of the CUPs and the calculated particle size for all of the polymer samples except for polymers below 15K. The CUPs based on polymer sample Poly-1 which theoretically has a number molecular weight of 3.5K shows considerable deviation in the experimental particle size as measured using DLS compared to the theoretical particle size. This indicates that there was some degree of aggregation of individual polymer chains during collapse. Stockmayer, has shown that for random free radical copolymerization, there is greater deviation in composition for shorter chains or low molecular weight polymers as compared to longer polymer chains. This would lead to a much broader distribution of methacrylic acid monomers in the polymer chain for low molecular weight MMA-MAA copolymers.[13] So, as the number average molecular weight of the polymer decreases, the average number of acid-groups on individual polymer chain from the methacrylic acid monomer also goes down. For Poly-2 which has a number average molecular weight of about 4.5K, a slight amount of aggregation was noted but it was far less than the Poly-1 polymer. All the polymers with molecular weight above 13K reduced to CUPs without any issue.

The polymers were synthesized based on a 9:1 molar ratio of acrylate group: acid group. So, statistically there was one unit of acid for every ten units in a polymer chain or a molecular weight of 973. So, for the poly-1 sample, the average weight of polymer chain is 3500 and hence it has about two carboxylic groups on average. But the molecular weight is a normal distribution and some polymer chains have a MW higher than the average and some polymer chains have a MW that is lower than average. So, some polymer chains have less than three carboxylic acid groups while some have more than three acid groups based on the molecular weight distribution and the random incorporation of acid groups. So when the polymer chains collapse, the chains with different molecular weight collapse to give CUP particles with different particle size and hence we get a particle size distribution for CUP particles. Figure 7 to Figure 15 represents the particle size distribution for the CUP particles for the various polymers synthesized with molecular weight ranging from 3.5K to 153K.

Table 5. Comparison of theoretical and experimental particle size of the CUPs.

Polymer synthesized	Particle size (nm)	
	Theoretical	Experimental
Poly-1	2.1	4.6
Poly-2	2.3	4.4
Poly-3	2.9	3.2
Poly-4	3.4	3.3
Poly-5	3.6	3.6
Poly-6	3.9	3.9
Poly-7	5.8	5.8
Poly-8	6.2	5.9
Poly-9	7.4	7.8

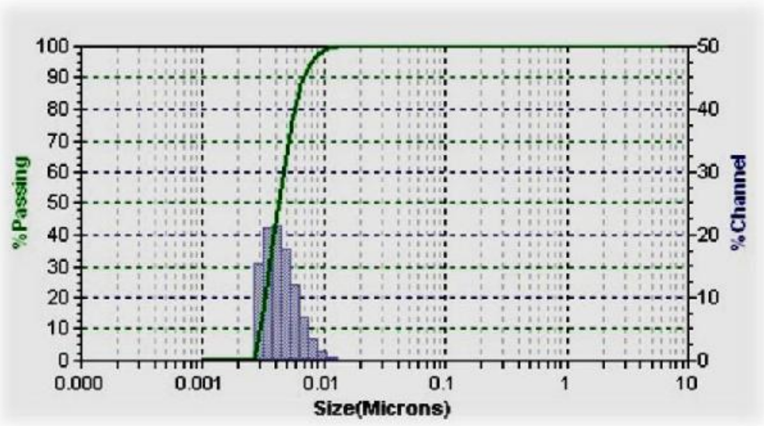


Figure 7. Particle size distribution of Poly-1 after filtering.

The Poly-1 sample has a molecular weight distribution and MMA incorporation that results in the number of hydrophilic (carboxylate) groups on the polymer chain to vary from anywhere between zero to about five depending upon the molecular weight of polymer chains. The polymer chains which do not have any hydrophilic (carboxylate) group will be highly unstable when exposed to water. So these chains precipitate out of the solution which is evident in Figure 3. These CUP solutions were filtered using a 0.45 micron filter, to get a clear, transparent solution. The filtered clear CUP solution of poly-1 was analyzed for particle size. The particle size distribution curve is shown Figure 7. No peaks are observed for particle size near the theoretical value of about 2.1 nm. The particle size was in the range of 3-10nm with an average value of 4.6 nm which indicated polymer aggregation. A percent solids test was done on the CUP solution before and after filtering to determine what percent of the polymer aggregated and precipitated out of the solution. The percent solids in CUP for poly-1 before filtering was 19.5% and after filtering it dropped to 12.5%. This shows that about 36% of the polymer chains were larger than 450nm.

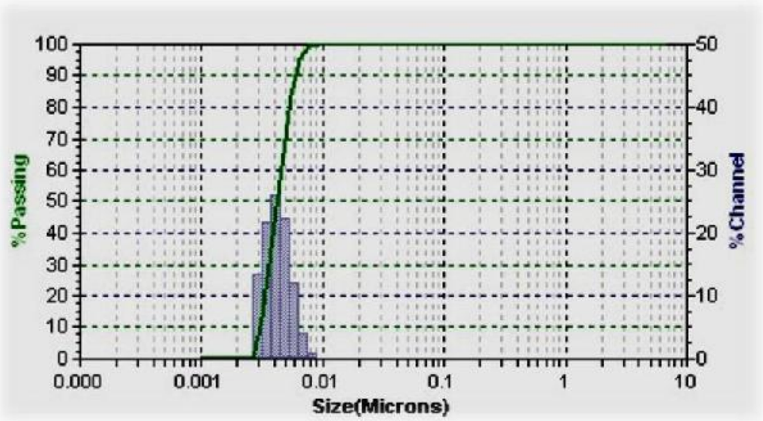


Figure 8. Particle size distribution of Poly-2.

From Figure 8, which shows the particle size distribution of CUP solution for Poly-2, we can see that the particle size was in the range of 3-9 nm. The average particle size was about 4.4 nm which was higher than the calculated value of 2.3 nm. Though the DLS instrument was capable of detecting particles as low as 0.8 nm, we don’t observe any particles below 3 nm in the particle size distribution curve for Poly-2 sample. The Poly-2 sample had a molecular weight distribution with an average molecular weight of about 4.5K. Therefore the number of carboxylate groups will also vary depending upon the molecular weight of the polymer chains. The four carboxylate groups or less on the polymer chain do no sufficiently stabilize CUP particles formed by the unimolecular collapse of polymeric chains. As a result, the polymer chains do not have sufficient stability from the electrostatic repulsion and aggregate during the collapse to form particles with larger particle size.

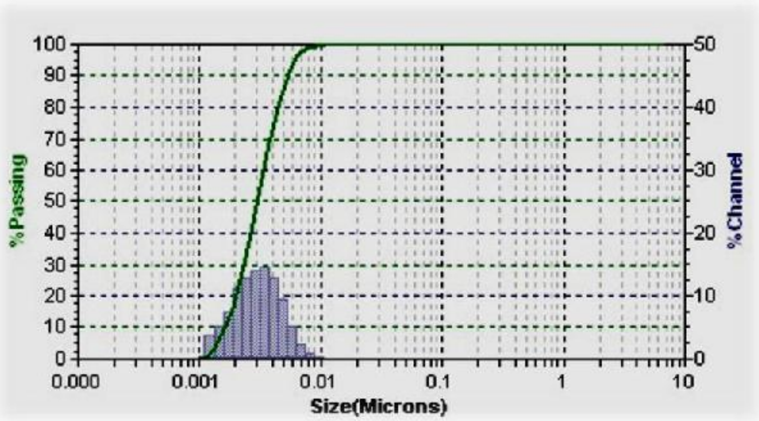


Figure 9. Particle size distribution of Poly-3.

Figure 9 shows the particle size distribution for Poly-3 sample (MW = 8.5K). The polymer chains have about eight carboxylate groups on an average with some chains having more and some less, again depending upon the molecular weight distribution. The distribution of particle size was broad with some aggregate formation. The experimental particle size (3.2 nm) was therefore somewhat greater than the theoretical value (2.9 nm). This could be possibly because of aggregation of polymer chains on the lower end of molecular weight distribution or carboxylate content. It should be noted that many of the chains did produce particles consistent with CUP formation.

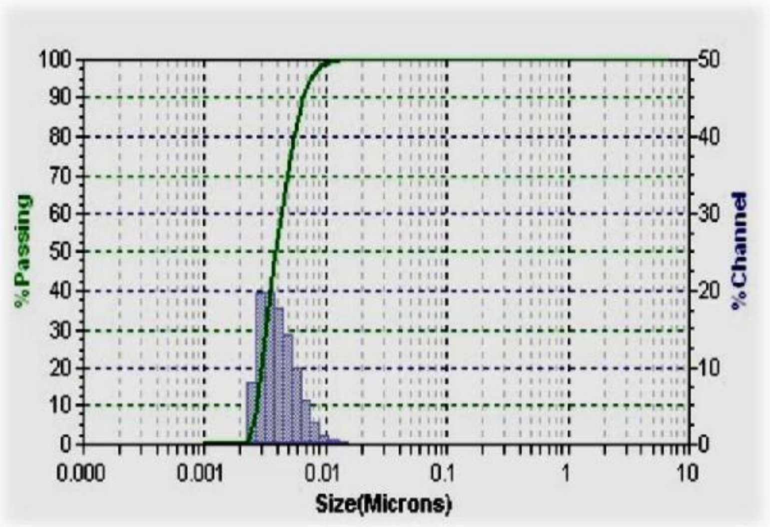


Figure 10. Particle size distribution of Poly-4.

Figure 10, Figure 11 and Figure 12 show the particle size distribution curve for CUPs prepared from Poly-4 (MW=13K), Poly-5 (MW=15K) and Poly-6 (MW=20K) respectively. The experimental particle size was in good agreement with the theoretical value. The particle size distribution were broad which is possibly due to the higher molecular weight fractions of the polymer samples which collapse to a particle of higher particle size. Size distribution for Poly-6 shows a bit of tail towards higher particle size which mainly is due to a higher concentration of polymer chains during the collapse. Diluting the polymer to 15% wt/wt in THF and then doing the water reduction might help to get rid of the tail. This will increase the average hydrodynamic distance between individual polymer chains and prevent aggregation during the collapse.

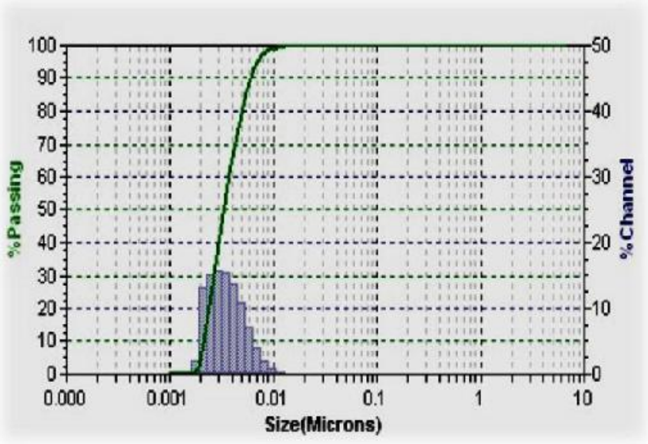


Figure 11. Particle size distribution of Poly-5.

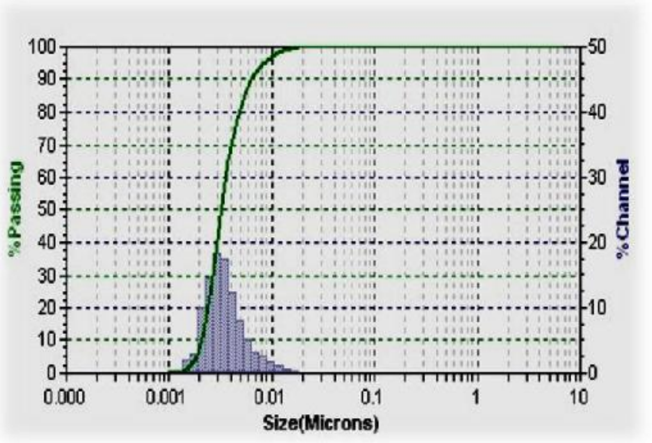


Figure 12. Particle size distribution of Poly-6.

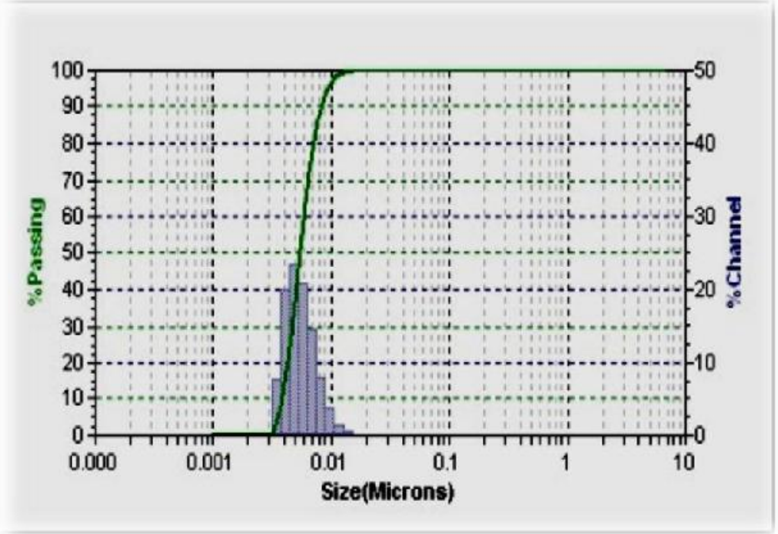


Figure 13. Particle size distribution of Poly-7.

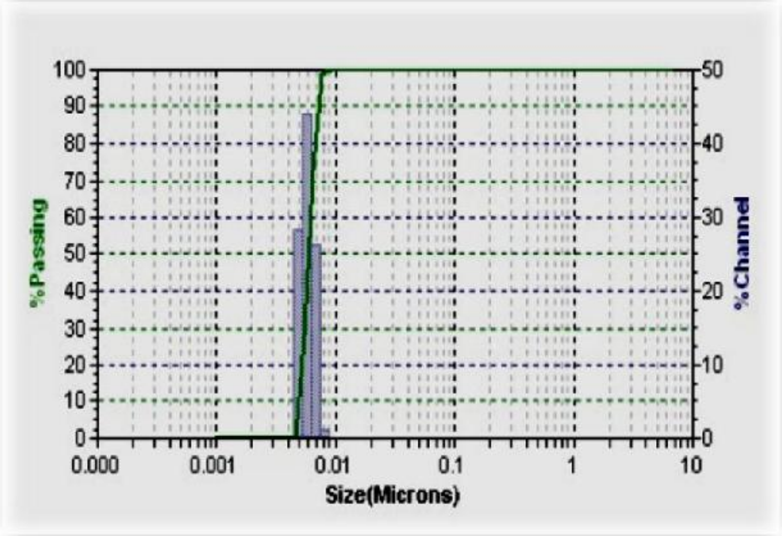


Figure 14. Particle size distribution of Poly-8.

The particle size distribution of CUPs prepared from high molecular weight polymers viz. Poly-7 (MW=72K), Poly-8 (MW=90K) and Poly-9 (MW=153K) are shown in Figure 13, Figure 14 and Figure 15 respectively. These polymers have large polymer chains with around 74 to 157 carboxylate groups respectively, on the chain which stabilizes the CUP particles. The experimental particle size was in very good agreement with the expected theoretical particle size with extremely low aggregation.

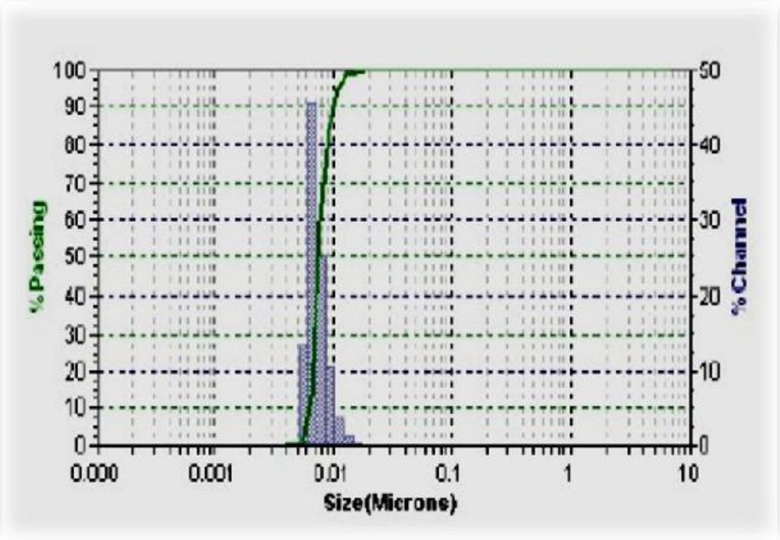


Figure 15. Particle size distribution of Poly-9.

In case of polymeric micelles, the hydrophobic core was protected from the aqueous environment by the hydrophilic corona and if the hydrophobic core gets exposed to water then the stability of micelle system is lost. The micelle loses its integrity and the polymer precipitates out.[24] In the CUP system, for the very low molecular weight polymer sample Poly-1 with average molecular weight of 3.5K, the hydrophilic groups are insufficient to prevent the contact of water with the hydrophobic polymer backbone chain. This causes precipitation of polymer. For CUPs based on samples Poly-2 and

Poly-3, with average molecular weight of 4.5K and 8.5K respectively, the hydrophilic groups are more than Poly-1 sample but still not sufficient to completely prevent contact of water with hydrophobic backbone. The CUP particles gain stability by aggregating which reduces the overall surface area and hence we see a higher particle size than the theoretical value. Polymers with molecular weight of 13k and above have sufficient number of hydrophilic groups on the polymeric chain which when water-reduced give CUPs with predictable particle sizes.

4. CONCLUSIONS

Colloidal unimolecular polymer particles were successfully synthesized from random copolymers of MMA and MAA. Transition from random coils to solid spherical particles occurs as the solvent environment was changed from a good solvent to a poor solvent for the polymer backbone giving rise to true nano-scale polymer particles with average particle size less than 10 nm. The particle size measurements using DLS prove that there is a molecular weight of the random copolymers below which the unimolecular collapse of polymer chains is not favored because of insufficient stability by way of electrostatic repulsion. This leads to some degree of aggregation of polymer chains at the collapse transition which is revealed from an increase in the particle diameter of CUPs as compared to the theoretical particle size. The polymers with a molecular weight of 13000 and above form CUPs with stable particle size which is consistent with the theoretical particle size. CUPs are formed with stable particle size and uniform size distribution even for molecular weights as high as 150k but at lower concentration. The size of individual polymer chains restricts the range of viable polymer concentration during the collapse to form colloidal unimolecular polymer particles. Unlike conventional water reducible resins, all CUP resins are VOC free except for the amine making them a very good candidate for future coatings applications, even as a lacquer.

5. ACKNOWLEDGEMENTS

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SECTION

2. CONCLUSIONS

The particle sizes and distribution of CUP measured from dynamic light scattering method were found to be consistent with the distribution of molecular weight of the copolymers which the CUP were water reduced from. The finding proved that the CUPs are unimolecular particles collapsed from polymer chains.

The rheology study of CUPs with different molecular weight indicated that water occupies significant volume fraction in CUP suspension and that the thickness of water layer on the surface of CUP shows a trend of increasing with particle sizes. The layers of surface water increase the effective volume of CUPs and thus have great impact on the rheology behavior of CUPs suspension. When CUPs suspension is in dilute to semi-dilute range ($\phi<0.08$), the viscosity of CUPs suspension fit well with Russel's model which includes primary, secondary and tertiary electroviscous effects. When the CUPs suspension is concentrated, the viscosity fit well with Krieger-Dougherty equation, from which the thickness and density were calculated.

Addition of electrolyte has significant effect on the rheology behavior of CUPs suspension. Results from capillary and cone-and-plate viscometer indicate that there exists a synergistic effect between percent solid of CUPs and added electrolyte on rheological behavior of CUPs suspension.

Surface activities of CUPs were found to increase with molecular weight, which possibly results from the increasing amount of surface active groups per particle with increasing molecular weight. The calculated area occupied by each particle was smaller than the largest cross-section area of CUP indicating that CUP particle barely sticks out of the liquid surface. It is highly possible that CUPs particle forms 2-D colloidal crystal on the water-N_2 interface.

The particle size measurements using DLS prove that there is a molecular weight of the random copolymers below which the unimolecular collapse of polymer chains is not favored because of insufficient stability by way of electrostatic repulsion. This leads to some degree of aggregation of polymer chains at the collapse transition which is revealed from an increase in the particle diameter of CUPs as compared to the theoretical particle size.

VITA

Minghang Chen was born in 1980 in Fujian, China. He obtained his Bachelor's degree in Environmental Engineering in July 2002 from Nanjing University of Science and Technology in Nanjing, China. In April 2005, Minghang obtained his Master in polymer science from the Tongji University, Shanghai, China. From April 2005 to December 2005, Minghang worked in SK Kaken coating in Shanghai as product developer. From Feb 2006 to June 2006, Minghang worked as technical assistant in General Electric Plastic in Shanghai. In August 2006, Minghang joined the Missouri University of Science and Technology to pursue a Ph. D degree in Chemistry. During the course of his Ph. D. work, Minghang has worked as a Teaching Assistant for the Department of Chemistry at MST, published three conference articles, submitted three articles for publication and presented his research work at one ACS annual meeting (September 2011) and one American Coating Conference (May 2012). He has received the award for "student presenter" at 2012 American coating Conference for his research presentation and "Shelby F. Thames Best Paper Award" in Feb. 2013 for conference paper.