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The synthesis and characterization of water-reducible nanoscale colloidal unimolecular polymer (CUP) particles

Cynthia J. Riddles

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THE SYNTHESIS AND CHARACTARIZATION OF WATER-REDUCIBLE

NANOSCALE COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES

by

CYNTHIA JEANNETTE RIDDLES

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PAPER II

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ABSTRACT

The coatings industry has adapted to more stringent guidelines in paint formulations. Current VOC (volatile organic compound) limits placed by the federal government have pushed the industry toward the development of paint formulations which have very little to no VOC's. The development of Colloidal Unimolecular Polymer (CUP) particles is a step in the direction of providing a resin system which exists in zero VOC aqueous dispersion.

The CUP particles are a part of the polymer field of Single Chain Nano Particles (SCNP) and ranged in diameters of 3-9 nm. The research presented in this dissertation describes the synthesis and design of these particles along with the various means of instrumentation used to gain insight into the structure and nature of these particles when suspended in aqueous medium.

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I would like to thank my advisor, Dr. Van De Mark for giving me the opportunity to pursue a doctorate degree, both financially and academically, and who has patiently pushed me to think on my own as my research progressed. Without the funding as a research assistant, pursuing a higher education would not have been possible being a single parent.

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NOMENCLATURE

Symbol	Description
CUP(s)	colloidal unimolecular polymer(s)
VOC	volatile organic compound(s)
THF	tetrahydrofuran
SLS	static light scattering
DLS	dynamic light scattering
AA	acrylic acid
MAA	methacrylic acid
BA	butyl acrylate
BMA	butyl methacrylate
TFEMA	trifluoroethyl methacrylate
DMAEMA	(dimethylamino)ethyl methacrylate
KHP	potassium hydrogen phthalate
AIBN	2,2′-azobis(2-methylpropionitrile)
MEK	methyl ethyl ketone
^{19}FNMR	^{19} fluorine nuclear magnetic resonance spectroscopy
NaOH	sodium hydroxide
KOH	potassium hydroxide
LiOH	lithium hydroxide
TMS	tetramethylsilane
^{1}H/^{13}CNMR	Proton/Carbon-13 Nuclear Magnetic Resonance Spectroscopy
GPC	gel permeation chromatography

T_g	glass transition temperature
T_1	longitudinal relaxation
T_2	transverse relaxtion
CPMG	Carr-Purcell-Meiboom-Gill sequence
M_n	number average molecular weight
ASTM	American Standards for Testing of Materials
nm	nanometer(s)
R_g	radius of gyration
SCNP(s)	single chain nano particle(s)
SEC	size exclusion chromatography
TDA	triple detector array
AN	acid number
CP-TOSS	cross polarization pulse sequence for total spin sideband suppression

INTRODUCTION

Water reducible resin technology has been used in the coatings industry since the 1950's. This technology is based on the nature of polymer chains to prefer to be entangled with each other than exist in a poor solvent condition. This idea has led to the discovery of a water reduction process which would result in single polymer chains collapsed into spheroidal particles on a nanoscale level. These were given the name Colloidal Unimolecular Polymer (CUP) particles. The CUPs are suspended in a VOC free aqueous media unlike the water reduced resins in coatings which contain water miscible co-solvents. The ability of the CUPs to exist in water without VOC's makes them a potentially beneficial resin technology.

The first part of this dissertation focused on the water reduction process. What factors influenced the reduction process, and what type of polymer design was necessary. Five polymers were synthesized with varying molecular weights. These were dissolved in THF, neutralized by ammonium hydroxide and water was added until a critical point was reached, and the polymer chains collapsed into CUP particles. Polymers were synthesized with varying molecular weights which were determined by SLS. The distribution curves from the SLS data were then used along with the density of the bulk polymer, and the equation of a sphere formula to determine the diameters that the particles would be. The polymers were then water reduced and particle size measurements were taken by DLS. The data from both SLS and the DLS were plotted together and showed a match to each other indicating that the particles collapse into

spheroid particles and that the diameters are able to be controlled by varying the molecular weight of the polymers.

The second part of this dissertation focused on determining if the CUP particles behaved similar to the bulk dry polymer. In order to accurately predict the particle size, calculations are made that use the density of the bulk polymer along with the equation of a sphere to give a particle diameter, therefore the density of the CUPs would have to be the same as that of the bulk.

The polymer used in the second publication was synthesized with the addition of trifluoroethyl methacrylate, a fluorine containing monomer for the purpose of ^{19}FNMR experiments. The polymer was water reduced, and it was hypothesized that the fluorine atoms would reside in the interior of the CUP particle after collapse due to the hydrophobic nature of the fluorine.

The T_g of the polymer was measured by DSC. This temperature was then used a guideline to measure T_2 relaxation through the glass transition. It was theorized that if the density of the CUP was the same as the bulk, a noticeable change in the T_2 relaxation time would be observed as the solution was heated up near the T_g. This increase in the relaxation time would be the result of the polymer chains increase in motion. The results of the ^{19}FNMR experiment were compared to an experiment made on the same polymer but in the dry bulk form. Both experiments showed an onset of a T_g occurring before the T_g measured by the DSC. The results were very close to each other, even though one experiment was using the dry bulk polymer, and the other used the CUPs suspended in aqueous media.

All polymers in this this dissertation were synthesized by free radical polymerization resulting in random copolymerization of acrylate and methacrylate monomers, some with acrylic acid and others with methacrylic acid. The ratio of non-ionizable monomers to acid monomers ranged from approximately 8:1 to 9:1 and followed the design of surfactant molecules found in the coatings industry having 16-22 carbon atoms making up the hydrophobic portion of the chain.

Other ratios of monomers above and below that chosen were investigated and found to water-reduce into CUP particles without difficulties; however, larger ratios of MMA, and larger numbers of acid monomers did not reduce well. The hydrophobicity of the monomers used determined the number of acid groups needed. For more hydrophobic monomers, such as n-butyl methacrylate or n-butyl acrylate, a ratio of 5:1 or 6:1 reduced well.

The final part of this dissertation was the investigation of using Group 1 metal hydroxides as the neutralizing agent. The use of ammonium hydroxide to neutralize the acid groups of the polymers led to successful CUP solutions. The drawback to ammonium hydroxide is that ammonia is released and if the CUPs are allowed to dry, then re-dissolve, the pH is non alkaline. A polymer was synthesized using MMA and MAA in a 9:1 ratio and three Group 1 hydroxides were used as the neutralizing agent. All were water reduced and the particle size was measured. They were then re-dissolved and measured again. These experiments are given in the Appendix.

PAPER

I.   SELF ASSEMBLY OF WATER INSOLUBLE POLYMERS INTO COLLOIDAL UNIMOLECULAR POLYMER (CUP) PARTICLES OF 3-9 NANOMETERS

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A. GRAPHICAL ToC
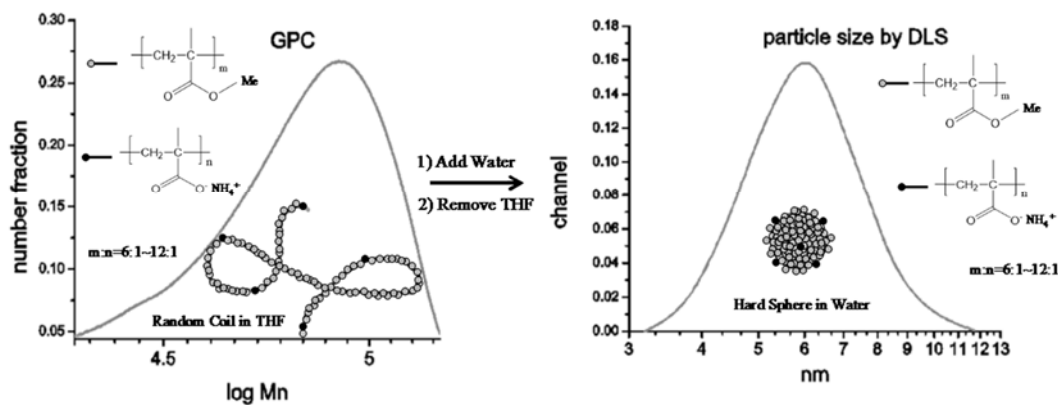
ABSTRACT

Colloidal Unimolecular Polymer, CUP, particles were synthesized and characterized as a potential new and useful spheroidal polymer conformation for a variety of applications. Also known as single chain nano particles, these nano materials are gaining in popularity. The route to CUP particle formation is an innovative approach utilizing a small number of hydrophilic groups along a hydrophobic polymer backbone which transitions from a random coil conformation in organic solvent to a hard sphere in water through a slow gradient with subsequent solvent removal. The CUP particles have diameters which are proportional to their molecular weights and range typically from 3 nm to over 9 nm. These CUP particles were stable in water and free of solvent or surfactants. The sodium or potassium salts of CUP particles are spheroidal and are able to be dried then re-dissolved in water with no aggregation, unlike the original polymer. The diameters of the CUP particles correlate with the absolute number average molecular weight (Mn) and distributions from the GPC. Molecular weights from 28K to 122K are reported here and are based on an acrylic copolymer having a molar ratio of 9:1 MMA:MAA.

Key Words: CUP, Colloid, Unimolecular, Polymer, Particle, Single Chain Nano Particle, Anionic

1. INTRODUCTION

The formation of Colloidal Unimolecular Polymers (CUPs) particles[1, 2] based upon the collapse of a single polymer chain from a good, low boiling, organic solvent through the action of a poor solvent such as water, should be possible based upon the simple Flory-Huggins theory. When the organic solvent is removed and the poor solvent remaining is water the resultant particle should be stable if it contains a sufficient number of stabilizing groups such as ionic or hydrophilic groups, analogous to that of a micelle. These CUP particles should follow a size distribution tracking that of the molecular weight distribution of the polymer.

The conformational behavior of polymer chains upon exposure to changes in the regional environment has been the focus of many studies. For uncharged polymer chains, Flory described the conformation of polymers in terms of a theta condition, either a theta solvent, or a theta temperature.[3] At the theta condition, he proposed that the polymer behaved as an ideal chain, and polymer/polymer interactions were balanced with polymer/solvent interactions, and the radius of gyration R_g was equal to the random walk configuration. A shift in either direction would cause the radius R_g to deviate from ideality due to either swelling in good solvent (greater than theta), or collapsing in poor solvent (less than theta). More complex conformational changes have been observed for charged polymers (polyelectrolytes) in solution.[4-7]

Several researchers have observed conformational changes in anionic or cationic homopolymers to show that a coil to globule transition occurred when there was a change in solvent dielectric.[4] A coil to an expanded chain conformation was observed by de Melo due to a change in pH.[5] Kirwan observed transitions from an extended chain, to a

pearl necklace conformation and then to a globule conformation, also by a change in the pH.[6] Kulkarni studied conformational changes that occurred in proteins when the pH was changed.[7] The functional shape a protein takes on by folding has been shown to be dependent on the sequence of the amino acids, and when the pH was shifted, a denaturing, or unfolding of the protein occurred.

The conformational behavior of polyelectrolytes has also led to the synthesis of polymers that had the ability to form single chain nano particles. These particles can mimic micelles and collapse inwardly due to a change in the regional environment, [8,9] or collapse by intramolecular self-crosslinking.[10-15] Li[8] investigated the use of multi-chain polymeric micelles as potential drug delivery systems. The hydrophobic blocks consisted of the anti-cancer drug paclitaxel, grafted onto blocks of polyether ester. These polymers were placed in an aqueous environment and upon adjusting the pH, the hydrophilic polyether ester portions of the chains oriented into the water phase, and left the hydrophobic paclitaxel oriented to the interior domain. These macromolecular polymeric micelles had an average diameter of 50 to 120 nanometers. The paclitaxel was able to be released into the cell through hydrolysis of the ester bonds that linked the drug to the hydrophilic exterior.

The micelle behavior of a single polyelectrolyte chain was observed by Morishima[9] when the chain collapsed, or 'self-assembled' in a poor solvent. Random copolymers were synthesized which consisted of roughly a 50/50 monomer ratio of hydrophilic monomer and hydrophobic monomer. At very low polymer/solvent concentration, the chains collapsed into unimolecular micelles of a diameter of approximately 5.5 nm. Both Li and Morishima[8,9] observed micelle-like behavior due

to polymer-solvent interactions, however, collapse of a single polymer chain can be made through intramolecular self crosslinking of the polymer chain. These single chain nano particles, or SCNP's had the ability to be tailored to specific sizes and shapes depending on the polymer chain functionality.

One focus of these nano particles has been on the synthesis of polymer chains containing reactive pendant groups which will self crosslink along the polymer chain leaving collapsed polymer particles.[10-15] Polymeric nano particles synthesized by Zhu et al[10], began with the living radical polymerization of methyl methacrylate with varying amounts of TMS protected enediyne containing methacrylate. Trimethylsilyl (TMS) was used as a protecting group during the polymerization to prevent unwanted Bergaman cyclization during the purification process. After purification, the polymer was then de-protected and treated in ultra dilute hot ether to induce Bergman cyclization. The resulting polymer particles were believed to be particles due to the significant drop of apparent molecular weights by GPC, and when analyzed by DSC, no measureable Tg was found which is indicative of a tight collapsed particle instead of a linear polymer chain.

Another example of nano particle synthesis was shown by Mercerreyes' et al.[11]who used linear copolymers which contained pendant acryloyl or methacryloyl groups as reactive precursors. Aliphatic polyester were obtained through ring opening (ROP) copolymerization of 4-acryloyloxy caprolactone with either ε-caprolactone or L,L- lactide rings, and also polystyrene copolymers derived by modification of poly(styrene-*co*-hydroxyethyl methacrylate) copolymers. These reactive precursors were radically polymerized in ultra-dilute conditions to give single chain nano particles

ranging in diameter of 3.8 to 13.1 nanometers. If polymerized in concentrate conditions, a 3-dimensional polymer network rather than particles was formed. The authors used Size Exclusion Chromatography (SEC) to show that the hydrodynamic volumes of the particles were significantly smaller than those of the linear polymer precursors, and DLS to measure the particle diameter.

The research of Altintas[12] et al took advantage of Diels Alder reactions by incorporating dienes precursors and dienophiles along the polymer backbone. The chains were then subjected to a UV-A fluorescent lamp at 320 nanometers causing intramolecular Diels Alder reactions to occur. These SCNP's were successfully created at concentrations of 0.017 mg/mL and the diameters were dependent on the molecular weight of the polymer precursors. The authors measured a change in the hydrodynamic diameter from the DLS instrument and also used AFM (atomic force microscopy) to show the polymer chains before and after crosslinking.

Hosonos[13] synthesized ABA triblock copolymers that when treated by heat the B block moieties folded into secondary structures. In a second step, the polymer was subjected to UV causing the A block moieties to orthogonally dimerize leaving a 3D structure. These structures can be tuned to resemble DNA structures to better aid in research. As with other SCNP synthesis, these particles were able to be achieved in dilute conditions at approximately 0.5 mg/mL.

Another example of SCNP synthetic methods is shown in the work by Murray and Fulton.[14] In this research the authors synthesized functional groups along the polymer chain, and then used a crosslinking agent to link the polymer chains intramolecularly. The authors then went another step and modified the chains with

monoacyl hydrazides and/or alkoxyamines. This could allow further reactions with other molecules to alter functionality on the outer areas of the particles. Again GPC was used to measure the difference in the retention times for both the linear polymer chains and the collapsed SCNP's.

Research by Jiang[15] et al showed SCNP's were achieved through the synthesis of sulfonyl azide functionalized polymer precursors. These polymers were then dissolved in benzyl ether and subjected to high heat causing the loss of nitrogen and forming nitrene groups which then reacted with the C-H bonds along the polymer backbone. The authors also used GPC and the change in retention times coupled with DLS to show collapse had taken place.

The synthesis of the above mentioned SCNP's were examples of techniques for tailoring polymer chains by placing reactive groups on the side chains and further reacting the chains in a fashion that promotes self crosslinking, or by the addition of a crosslinking agent to intramolecularly crosslink. In all the examples given, the final product was shown to be 'unimolecular' or as termed single chain nano particles SCNP's formed by either intramolecular self crosslinking, or the inherent behavior of polymer-polymer interactions overcoming polymer-solvent interactions.

Non-unimolecular collapse has been observed in waterborne urethane resins used in the coatings industry. Resins have been synthesized by the reaction of isocyanates with either modified or unmodified polyester polyols, in acetone with water addition. Removal of the acetone from the resin water blend caused the chains to collapse into aggregate particles with diameters of approximately 25 nanometers.[16] Collapse of polymer chains while still entangled has also been used in the coatings industry, as water-

reducible resins.[17] Water-reducible resins were dissolved in high boiling water miscible solvents, the resins contained ionizable carboxylic acid groups that were neutralized with amines.   Water was then added to the coating, until the solvent blend became a less-than theta solvent condition, which caused the chains to collapse.

Our CUP particles although similar in concept to Morishima[9] are also unique due to the process of dissolving the polymer first in a water miscible organic solvent, adding water, then evaporation of the organic solvent from our solutions, leaving the CUP particles suspended in aqueous media, thereby achieving a VOC (volatile organic compound) free solution. This is especially important due to the fact that in and of themselves, the particles are not water soluble, however after the water reduction process are suspended in water and are stable long term.

At this time, GPC has been used in our research only to obtain absolute Mn molecular weights of the starting polymer chains. Most research of SCNP's showed that the collapse of these particles takes place in the solvent that the polymer is dissolved in. This allows the authors to use a change in retention times in GPC to show a decrease in the size, as shown by an increase in retention times. This coupled with DLS measurement of the diameters in the solvent allowed proof of the collapse of the polymer chains to SCNP's. Our CUP particles are first dissolved in a water miscible solvent and are random coils. After the acid groups are neutralized, water is added and the polymer chains collapse. The solvent is then stripped off leaving particles suspended in water. At this point they are spheroidal in shape. Two separate light scattering techniques, GPC SLS and DLS, show that the collapse of the polymer chains has taken place.

Static light scattering (SLS) was used for absolute molecular weight, and dynamic light scattering (DLS) was used to measure the diameter of the CUP particles. The SLS data was used to calculate the theoretical diameter each polymer chain should collapse to, and this was compared to the experimental particle size data from the DLS instrument. The term Colloidal Unimolecular Polymer has been introduced to describe these solid spherical single chain particles suspended in the continuous VOC free aqueous phase.

The design of polymers capable of unimolecular collapse into spheroid-like particles was complex and many factors were considered. The most basic requirement was the balance between the hydrophobic and hydrophilic groups on the polymer chain. An over-abundance of hydrophilicity caused the polymers to remain water soluble, whereas a lack of sufficient amount of hydrophilicity caused the polymers to be so hydrophobic that precipitation occurred in the presence of any amount of water. Both extremes prevented unimolecular collapse. The hydrophobicity of the monomer, flexibility and the location of both hydrophobic and hydrophilic groups on the monomer had to be considered. Another requirement for successful CUP formation was that the polymer chain had to have enough flexibility to accommodate the changing conformation, while allowing association of like groups along the chain to take place. The use of charged groups enhances the hydrophilic nature while offering the added benefit of ionic forces.

2. EXPERIMENTAL

2.1 Materials

Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. MMA was purified by washing with a 10% (w/w) solution of sodium bicarbonate, followed by rinsing with de-ionized water, and brine. The product was dried over sodium sulfate and filtered. Copper (I) bromide was added to the MMA as an inhibitor, and simple distillation under nitrogen was carried out. MAA was purified by distillation with copper (I) bromide under reduced pressure. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received.

2.2 Polymerization

All polymers were synthesized by the same method of free radical polymerization in methyl ethyl ketone (MEK) and are listed in Table 1, differing only in the molar ratio of dodecanethiol to monomers, to produce a range of molecular weights. To a 2000 ml three-neck flask was added 750 grams of MEK and a magnetic stirring bar. The monomers were then added; 225.25 g (2.25 mole) of MMA, and 21.50 g (0.25 mole) of MAA, giving a molar ratio of 9:1 MMA/MAA. Dodecanethiol in the amount of 2.15 g (10.62mmole) was added a 1:235 ratio, and finally AIBN 0.30 g (1.83mmole). The flask was fitted with a nitrogen line, condenser, and a gas outlet adapter connected to an oil bubbler to allow a positive flow of nitrogen throughout the polymerization. The flask was heated slowly to reflux and allowed to react for 24 hours. The polymer solution was

then cooled to room temperature, and precipitated in cold deionized water under high shear, then dried under reduced pressure.

2.3 Instrumental Techniques

The ^{1}HNMR was carried out using a Varian 400 MHz FT/NMR spectrometer using 5 mm o.d. tube. Sample concentrations were approximately 20% (w/v) in CDCl₃. All spectra were consistent with proposed polymer structure of PMMA/MAA. 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). Particle sizes 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. Acid numbers (AN) for all polymers were measured by titration method ASTM D 974 and are shown in Table 1; the method was modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, tetrahydrofuran (THF) to dissolve the samples and phenolphthalein in place of methyl orange. Viscosity measurements were done by Ubbelohde viscometer method ASTM D 446-07. Additional viscosity measurements, when needed, were made with an LV DVIII rheometer with spindle CP-40 from Brookfield Engineering.

Table 1. Thiol Ratio, Percent Yield, and Acid Number

Polymer	Thiol Ratio	Percent Yield	Theoretical /Measured AN mg KOH/g polymer
1	1:235	82.3	56.8/59.1
2	1:500	86.9	56.8/57.7
3	1:600	88.1	56.8/58.0
4	1:763	84.2	56.8/59.7
5	1:878	81.0	56.8/59.7

Table 2. Molecular Weight, Polydispersity and Mark-Houwink Data

Polymer	Mn (kg/mol)	Polydispersity	Mark Houwink Data	
			LogK	a
1	28	1.24	-4.42	0.76
2	36	1.24	-4.12	0.67
3	58	1.28	-4.42	0.76
4	106	1.59	-4.64	0.71
5	122	1.47	-5.04	0.76

2.4 Water-Reduction Method

Lower molecular weight polymers 1-3 were dissolved in THF (20% w/w) and polymers 4, and 5 were (10% w/w) and stirred overnight. Ammonium hydroxide was added to neutralize the acid groups, to an approximate pH of 8.5 ± 0.2. De-ionized water at pH 8, 2.25 times the weight of THF used, was added by a peristaltic pump in the rate of 1.24g/minute. After the water was added, the THF was stripped off in-vacuo. The clear solutions were then filtered with a 0.45 micron filter to remove any extraneous trace contaminants, and particle sizes were measured. The typical loss on filtering was less

than 0.05% of the solids. Fig. 1 illustrates a typical distribution graph from the DLS instrument.
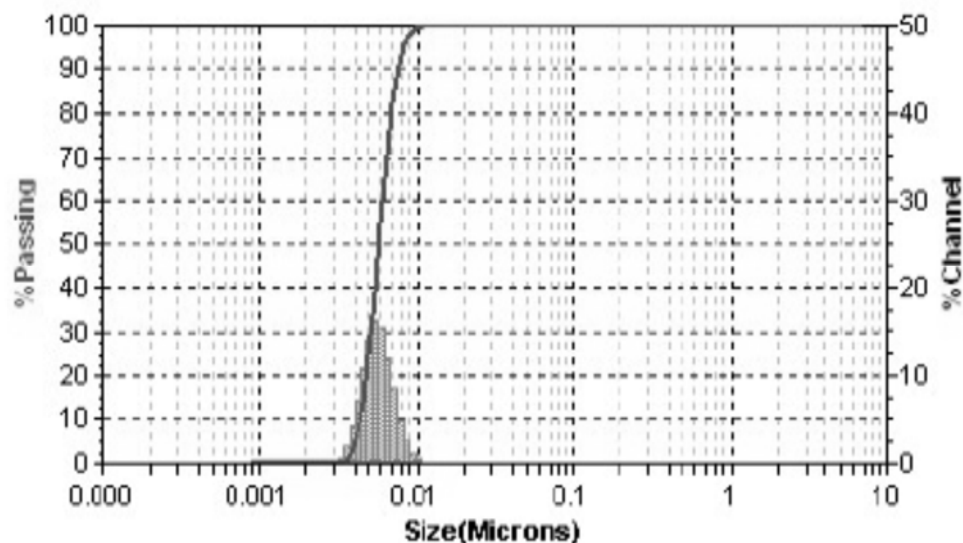
Fig. 1. Polymer 3 particle size distribution by DLS

3. RESULTS AND DISCUSSION

3.1 Polymerization of MMA and MAA

Reactivity ratios of both MMA and MAA have been reported in the literature in acetone[18]. These values were: $r_1 = r_{MMA} = 0.32$ and $r_2 = r_{MA} = 0.63$, which gave $r_1 r_2 = 0.20$, and showed relatively random copolymerization occurred. Drastic deviations from the reactivity ratios being in MEK rather than acetone were not expected and random copolymerization of MMA and MAA in MEK were predicted.

The synthetic approach of the polymers in this research more closely resemble the behavior of micelles, the 9:1 molar ratio of MMA/MAA was based on typical surfactants having approximately 16-22 carbon atoms comprising the hydrophobic portion of the chain to one hydrophilic group.[19] Other ratios of monomers above and below that chosen were investigated and found to water-reduce into CUP particles without difficulties; however, larger MMA values, above 12 produced more coagulum. If the MAA fraction increases, the polymer may produce other conformations or become water soluble when reduced. The hydrophobicity of the monomers used determined the number of acid groups needed. For more hydrophobic monomers, such as n-butyl methacrylate or n-butyl acrylate, a ratio of 5:1 or 6:1 reduced well. Due to the random nature of the polymerization mechanism, it was not possible to place one MAA monomer at every 10th position. The combination of controlling the monomer ratio and the random placement of the acid groups was sufficient to produce the CUP particles.

The synthetic routes to produce SCNP's involve the synthesis of the polymeric precursors and many require controlled radical polymerization techniques such as ring opening polymerization (ROP)[10], reversible addition-fragmentation chain transfer (RAFT)[11], nitroxide-mediated radical polymerization (NMP)[12], atom transfer radical polymerization (ATRP)[13]. This first step of the synthesis then typically requires a second step to further react the pendant reactive moieties in a manner that promotes self crosslinking. The polymer only required radical polymerization techniques.

3.2 Formation of CUP Particles

Water-reducible polymers display a unique viscosity curve during the reduction

process.[20] Polymers undergo transitions from random coil when dissolved in solvent,

to an extended chain with addition of water due to the ionic repulsion along the chain,

and finally, to a collapsed state, resulting in a pronounced drop in viscosity. This

transition is also observed by an increase in retention times in GPC using polystyrene

standards of known molecular weights and is used widely to show that collapse of a

polymer chain has occurred.[10-15] Just as the viscosity curve shows a marked drop in

viscosity, the GPC will show a marked decrease in the apparent molecular weight of the

polymer when collapsed. The CUP particles in this research were not able to be

evaluated by the typical GPC methods used by others due to the fact that when the

polymer is a random coil configuration it exists in THF but after collapsing into spherical

particles, they are suspended in water. For this reason GPC was used in conjunction with

SLS detection to give absolute molecular weights only, but the viscosity was measured

for a sample polymer to aid in showing there was a point where collapse occurred.

The viscosity of polymer 3 was measured during the water reduction process to

show the sharp drop in viscosity that occurred at the collapse point as seen in Figure 2.

When ammonium hydroxide was added to the solution at 20% solids, the viscosity

increased slightly due to the ammonium carboxylate salt inter and intra polymer ionic

interactions and hydrogen bonding. As water was added, solvation of the ammonium ion

and carboxylate groups occurs. As more water was added, the viscosity increased due to

the repulsive force of the carboxylate groups causing the polymer chains to take on a

more rod-like conformation. At a critical point where the polymer/polymer interactions

overcame the polymer/solvent interactions, the polymer collapsed into spheroid particles as was evidenced by the dramatic drop in viscosity.
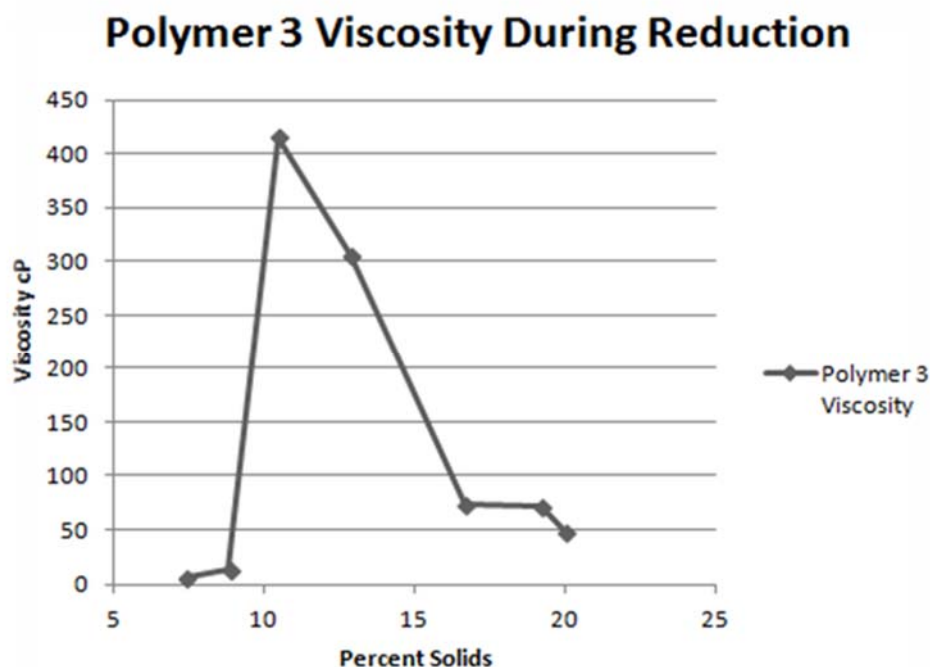
Fig. 2. Viscosity of polymer 3 during water reduction

Pictorially, this dramatic drop in viscosity is shown in Figure 3, with III going to IV. The hollow spheres represent the hydrophobic polymer backbone and the solid spheres represent the ionizable carboxylic acid groups **I**. When base, in this case, ammonium hydroxide was added to the solution, the acid groups form salts **II**, likely as intimate ion pairs. As water was added the ammonium carboxylate salt ions become solvated and separate **III**. These carboxylate groups then repelled each other due to the increasing dielectric caused by the added water and the chain extended toward linearity which increased the viscosity. At a critical point, collapse of the polymer occurs with the

carboxylate groups oriented into the water phase, organizing to produce maximum

separation of charge and the hydrophobic polymer chain collapsed into a spheroidal CUP

particle **IV**.   The removal of the THF yields the final CUP particles free of solvent, **V**.
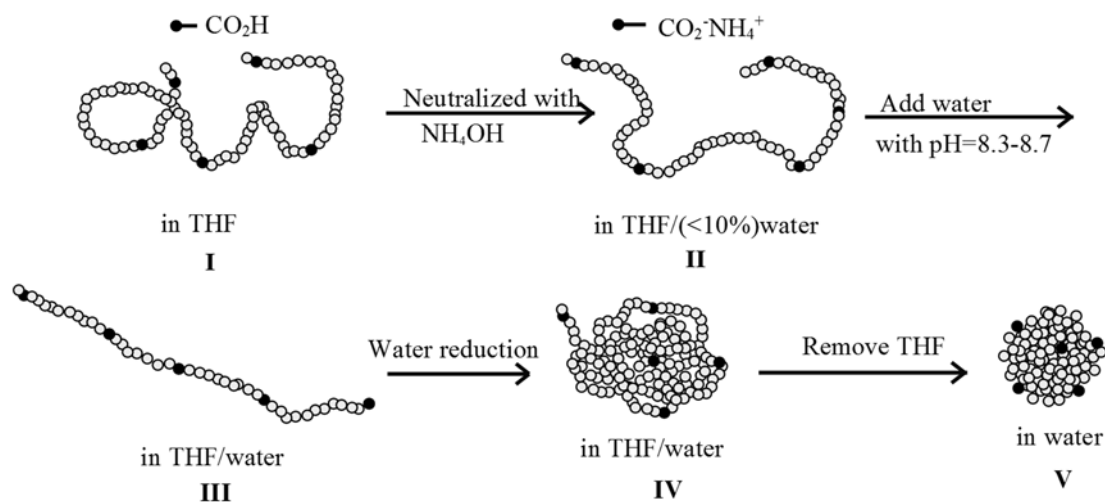
Fig. 3. General water reduction process. **I**. Random coil configuration in THF. **II** Random coil intimate ion pair. **III**. Extended coil solvent separated ion pair. **IV**. Collapsed coil. **V**. Hard sphere.

The water reduction process was analogous to that of micelle formation. As water

was added to the polymer/THF solution, the solvent organized around the hydrophobic

backbone of the MMA units, similar to that of surfactant molecules prior to formation of

the micelle. The collapse of the chains into CUP particles was in part driven by the

release of the organized water to the bulk increasing the entropy. The same occurs during

micelle formation, which at first glance seems to be disfavored due to the loss of entropy

caused by multiple surfactant molecules organizing into a single micelle. The entropy

loss is due to molecular organization from the surfactant molecules, but overshadowed by the gain in entropy when the organized water surrounding the surfactant molecules is released to the bulk.[21,22] The CUP particles approximate a sphere like shape due to the carboxylate group's repulsive nature to each other. These CUP particles are small enough that Brownian motion keeps the particles suspended and thus are thermodynamically stable unlike the larger latex particles, which settle with time. Samples of the CUP particle suspensions have been retained for over three years with no change in particle size and no aggregation or settling.

3.3 Particle Size Analysis

An important tool for measuring the diameter of collapsed polymer particles in solution is dynamic light scattering DLS. This method has been used in conjunction with the GPC and is widely accepted as evidence of polymers existing in a collapsed particle state. [10, 12, 14, 15] The DLS instrument first measures the diffusion coefficient of the particles in the media, and then calculates the particle size by the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r} \tag{1}$$

Where k_B is the Boltzmann constant, T is the absolute temperature of the solution, η is the viscosity of the solvent and r is the radius of the particle. In this research, the particle size of the CUP's was measured using the Nanotrac 250 dynamic light scattering instrument. Unlike most SCNP's, our CUP particles are charged, and therefore the light scattering method chosen needed some justification. First, the particle size was about 3-9 nm, very small compared with the working wavelength of the laser signal (780nm),

therefore the signal of scattered 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 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 equation 1 no longer valid. One of the frequently used methods has been to correct equation 1 with reduced osmotic pressure $(\frac{\partial \pi}{\partial c})$T. Since measuring the osmotic pressure of colloid dispersion is very time-consuming, it is not a convenient method. Therefore, another method was employed.

The relationship between the viscosity and the diffusion coefficient has been extensively studied from the classical Stokes-Einstein model which is valid for a dilute system. When higher concentrations are involved, the relationship is more complicated. A generalized Stokes-Einstein relation (GSE) has been derived by many researches.[23] At various volume fractionsϕ, the relationship between zero-limiting shear viscosity $\eta(\phi)$ of the solution and the long-time self-diffusion coefficient $D_L^S(\phi)$ can be represented by

$$\frac{\eta(\phi)}{\eta_0} = \frac{D_0}{D_L^S(\phi)} \qquad (2)$$

Or

$$D_L^S(\phi) = \frac{kT}{6\pi\eta(\phi)r} \qquad (3)$$

equation 2 or 3 which have agreed well with experiments in solid PMMA[24], micelles[25], and silica[26]. In the case of charge stabilized silica[27], the approximation

was good in the dilute range (volume fraction is less than 0.1). For higher volume

fractions, the hydrodynamic interaction between charged particles is far larger than

Brownian motion from solvent molecules; 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. This procedure works well for dilute suspension

with big particles. However, the volume fraction of CUP required was approximately

0.08 to obtain a high enough scattered light intensity, far away from infinite dilution.

Therefore the diffusion coefficient measured by the instrument was no longer D_0, or the

self-diffusion coefficient, but $D_L^S(\phi)$, the collective diffusion coefficient. In other words,

equation 3 instead of equation 1 should be used to calculate the particle size. This

validates the need for the viscosity of solution to be entered in order to calculate particle

size rather than the viscosity of the pure solvent.

Prior to measuring the particle size, the loading index of CUP solution in

Nanotrac 250 was measured to make sure the concentration was high enough to get a

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[28] model as

$$\sqrt{\tau} = \sqrt{\tau_0} + \sqrt{\eta D} \tag{4}$$

where τ is the shear stress, τ_0 is the yield stress, η is the plastic viscosity, D is the shear

rate. If τ_0 was zero, it represented a 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 a power law model as

$$\tau = kD^n \qquad\qquad\qquad (5)$$

where k is consistency index with units of centipoise, and n is the flow index. The more n
deviates from 1, the more shear-thinning, n<1 or shear-thickening, n>1 will the fluid be.
The viscosity used to enter into the DLS software was the value of the consistency index,
which was also the viscosity of the fluid at a shear rate of 1 Hz.

3.4 Role of the Solvent

The purity of the water was a critical variable for the reduction process. The
presence of polyvalent ions such as calcium can result in aggregation of the resin causing
the solution to be opaque due to light scattering. There are two possible reasons for this
observation. The first one is interchain bridging. The polymer chains before collapsing
are extended and bear negative charges. When bivalent cations, i.e. calcium ions, interact
with the carboxylate groups on the chains it can cause multiple chains to aggregate and
fall out of solution. The second possible reason is that the calcium salt of carboxylic acids
do not readily dissociate so that the polymer chain loses its ability to be stabilized and
precipitates from solution. As little as a few parts per million of calcium can cause the
water reduction to produce larger particles.

The experimental protocol for the reduction was very important. The water was
added dropwise by a peristaltic pump through a submerged tube slowly to avoid a large
regional solvent compositional change. If the water was allowed to be added too quickly

or dropwise on the surface of the polymer/THF solution, coagulum formed. The stirring rate was also maintained at a modest rate to avoid large regional solvent compositional change. Any stoppage in the stirrer will result in the formation of coagulum and usually a hazy solution. If performed correctly the solution remains clear with no opacity. It should be noted that these acrylic copolymers and their ammonium salts are all water insoluble if not in the form of a cup particle.

THF was selected as the dissolution solvent due to its excellent solvency for acrylics, its miscibility with water, and low boiling point which allow it to be easily stripped off without loss of significant amounts of water. For polymer **5** the viscosity of a 10% solution in THF was measured by a Brookfield DVIII rheometer.   As the amount of added water was increased, the viscosity was again measured to determine the critical collapse point. At a volume ratio of approximately 60% water to 40% THF the polymer collapsed. The important point regarding this was that only when the ratio reaches or exceeds this solvent composition that the polymer will collapse. At this point the polymer chain undergoes a radical transformation from an extended coil to a collapsed sphere shape and the viscosity will sharply decrease.

One complication, which was found to affect the ability of the chains to collapse in a unimolecular fashion, was the concentration of the polymer chains at the collapse point. If the chains were at a high concentration, they collapsed while entangled, resulting in diameters which were larger than expected. If the concentration was low the individual polymer chain was able to collapse on itself. This concentration dependence was also seen in other researcher's work.

Mercerreyes[10] predicted that at certain concentrations above what he termed C_{eq} only intermolecular collapses took place, and below that value, intramolecular collapse occurred and at intermediate concentrations both took place. Successful collapse in a unimolecular fashion was found to occur at concentrations below 10^{-5} M and is approximately 1mg/mL for a polymer having a molecular weight of 100K. Altintas[12] investigated concentrations of 0.133, 0.067, 0.033 and 0.0117 mg/mL. Of these, 0.017 mg/mL produced unimolecular collapse proven by a clean SEC trace and found no bimodal distributions. Murray[14] found ~0.1 mM concentrations were optimal, for a polymer of 100K this would be 10 mg/mL. Jiang[15] found that for their SCNP's, the range of 1-10 mg/mL was successful. For our CUP particles, the concentration initially begins above 100 mg/ml for polymers above 40K and 200 mg/mL for polymers below 40K. The polymers collapsed when the ratio of THF/water reached a 60/40% (w/w) which would be a concentration of 60 mg/mL and 120 mg/mL respectively at the collapse point. The solvent was then stripped off leaving the CUP particles in roughly a 100 mg/ml polymer in water solution. The final solution can be concentrated through water evaporation after reduction to form CUPs without altering the particle size or distribution.

For water-reducible resins typically used in coatings, the collapsed state may be composed of multiple chains due to the high concentration of polymer chains present at the collapse point. The water reduction process used in this research was conceptually similar to this process; however, two important differences should be noted. First, this research was focused on unimolecular collapse through low concentration at the reduction point, and secondly, the solvent was stripped off leaving the particles suspended in water, organic solvent free.

At the solvent ratio where Polymer **5** collapsed, the Hansen solubility parameters were calculated and compared with two solvents, ethanol and methanol, where δ_t is the total Hansen solubility parameter, δ_d, δ_p, δ_h are the parameters for the dispersive, polar and hydrogen bonding contributions, and φ_1 and φ_2 are the volume fractions for each solvent.

$$\delta_t^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \tag{6}$$

$$\delta_d = \delta_{d1}\varphi_1 + \delta_{d2}\varphi_2 \tag{7}$$

$$\delta_p = \delta_{p1}\varphi_1 + \delta_{p2}\varphi_2 \tag{8}$$

$$\delta_h = \delta_{h1}\varphi_1 + \delta_{h2}\varphi_2 \tag{9}$$

Table 3 lists the values for the four solvents taken from Handbook of Solubility Parameters[29]. Table 4 gives the volume fraction parameters calculated for the solvent blend at the collapse point.

Table 3. Hansen Parameters[29]

Solvent	δd	δp	δh	δt
THF	16.8	5.7	8	19.4
Water	15.6	16	42.3	47.8
Methanol	15.1	12.3	22.3	29.6
Ethanol	15.8	8.8	19.4	26.5

Table 4. Volume Fraction Hansen Parameters for Solvent Blend

Solvent/Fraction	δ_d	δ_p	δ_h	δ_t
THF/0.42	7.1	2.4	3.4	
Water/0.58	9.0	9.3	24.5	
Blend Total	16.1	11.7	27.9	34.3

The solubility parameters for the solvent blend for polymer 5 at the collapse point were found to be closer to methanol than ethanol, which was consistent with the polymer being insoluble in methanol, and soluble in ethanol when heated.

It should be noted that in this system, the collapse occurred while adding the water but if a higher THF concentration were used, the critical point would not have been reached with this amount of water, the collapse would have occurred while the THF was being stripped off. Collapse only occurs when the amount of water exceeds the critical water to THF ratio. The polymer concentration, when collapse occurs, was dependent upon the amount of THF used and added water to reach the collapse point.

The reduction of polymer 3 with ammonium hydroxide resulted in a clear solution and when dried was a brittle crumbling material which powdered easily. When placed back in pH 8.5 water, the powder partially returned to solution with some aggregation. The small amount of aggregation was likely caused by loss of ammonium from the salt rendering the area less hydrophilic causing aggregation sites. However, when the same polymer was reduced with sodium or potassium hydroxide as the base, the dried polymer was able to completely return to the fully dispersed state with an identical particle size distribution as before drying. This indicates that the CUP salts are stable when dried and can be easily re-dispersed. It should be noted that polymers that have a T_g lower than ambient cannot be reconstituted due to irreversible entanglement when dried. Figure **4** shows the reduced sodium salt of polymer **3** as a dried powder, and the reconstituted dispersion of CUPs.
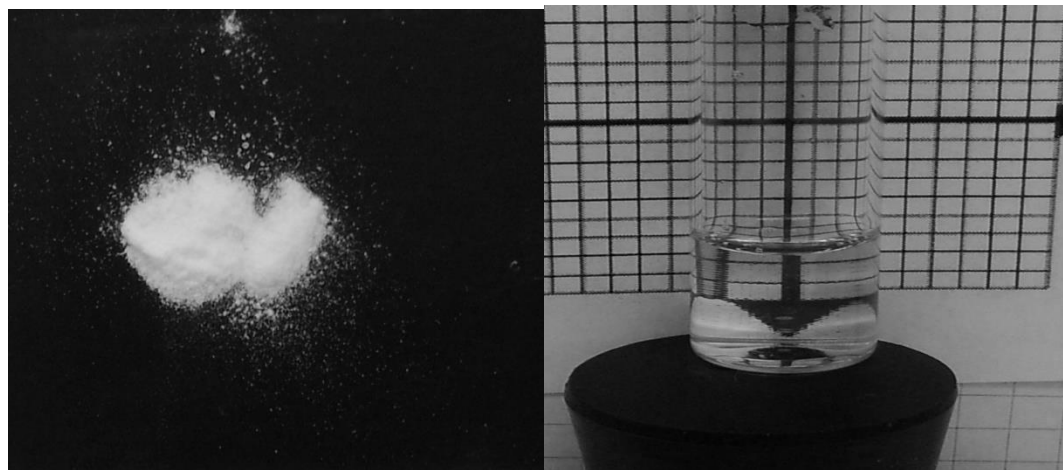
Fig. 4. Polymer 3 CUP dried and powdered (left) and re-dissolved/dispersed (right) in water

After water reduction and removal of the THF, the solution was allowed to dry on a watch glass. As can be seen from Fig. **5**, the CUP particles, polymer **3**, do not form a film but crack analogous to that of a high T_g, 50°C, latex. Spherical or spheroidal particles should pack into hexagonal close packing and thus would have cleavage plains. The normal size distribution of the particles will result in a less than perfect lattice.
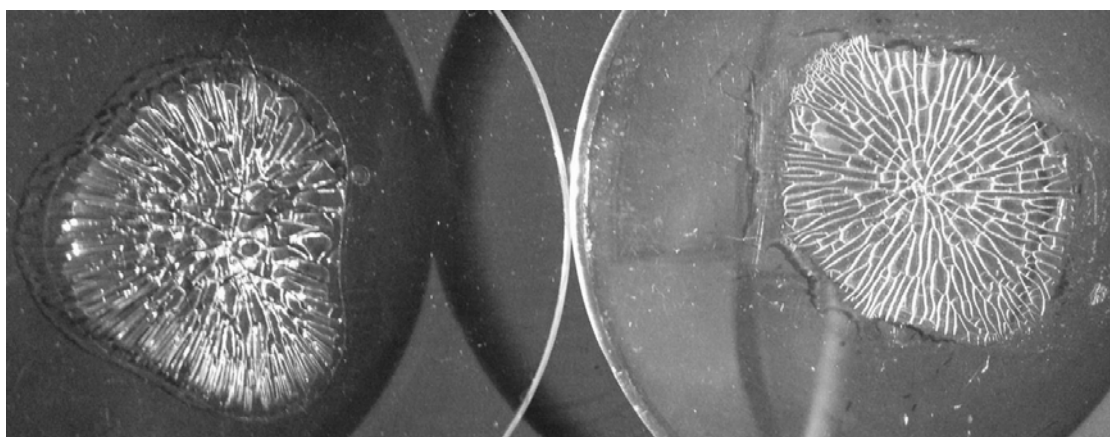
Fig. 5. Dry fractured patterns of CUP (left) and high T_g latex (right)

3.5 Conformation of the CUP Particles

A polymer containing many ionic groups can theoretically form many

conformations depending on the charge density along the chain.   A widely accepted

theoretical model was based on an electrostatic blob and the scaling theory first

developed by de Gennes and Pfuety and reviewed by Dobryinin.[30] The scaling theory

assumes a polyelectrolyte in a poor solvent takes on a pearl necklace shape, with the

'pearls' being electrostatic blobs. For a neutral polymer in a poor solvent such as water,

the polymer collapses into a spheroid globule. When charges are present, the globule

becomes an elongated electrostatic blob, and then forms the pearl necklace shape,

depending on the fraction of charges in the blob, the dielectric of the solvent, and the

temperature. A theoretical model has been developed in which a polyelectrolyte

undergoes several conformations from an electrostatic blob, to a dumbbell and to a

necklace of three pearls.[31] In this model, a dilute solution of a polyelectrolyte of

uniform charge was considered, having a degree of polymerization N, monomer size b,

and fraction of charged monomers f in a poor solvent having a dielectric of ε. The

following predictions are made for a polyelectrolyte of N=200 monomers at three

different charge densities (f):

f = 0.000   spherical globule,

f = 0.125   dumbbell shape,

f = 0.150   pearl necklace with three beads.

When the polymer is uncharged, collapse into a spherical globule will be observed. When an electrostatic blob contains a fraction of charged monomers equal to 0.125, the electrostatic blob separates into a dumbbell shape, and at a fraction of 0.150 a necklace of three pearls will exist. The CUP particles presented here were on the lower edge of the theoretical model. Pearl necklace conformations were not observed, and could be due to the low charge fraction, the chains were 9:1 MMA: MAA, meaning 10% of the polymer chain would be ionizable. If the acid groups were neutralized 100% by the ammonium hydroxide, the resulting charge fraction would be 0.10. The actual formal charge may be even lower than 0.1 due to charge condensation on the surface of the particle. Aseyev observed a coil to globule transition rather than a dumbbell or pearl necklace conformation for a polycation polyelectrolyte and measured the viscosity and both the hydrodynamic radius and radius of gyration as acetone was added to water.[4] The authors found that when the mass fraction (γ) of acetone was below 0.80 the viscosity of the solution displayed typical polyelectrolyte behavior, but when $\gamma > 0.80$ collapse of the polycation into a globular state occurred.

The CUPs in this research were not of the pearl necklace conformation and was evidenced by the measured particle diameters being very close to the calculated diameters. The pearl necklace conformation would cause an increase in the diameter of the particles, due to the length of the 'necklaces' as depicted in Fig. **6**, $D_1 > D_2$.
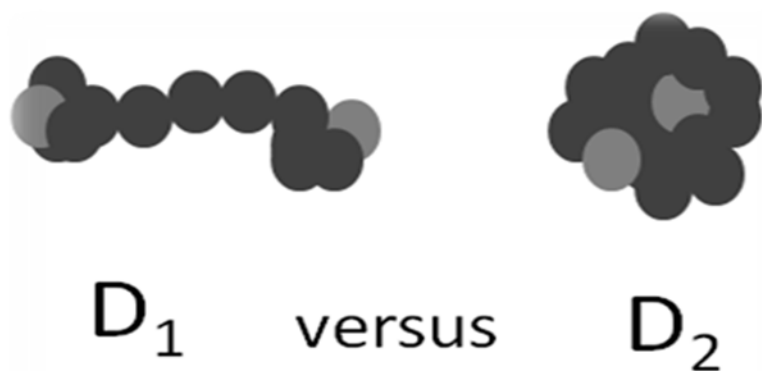
Fig. 6. Depiction of pearl necklace diameter

3.6 Unimolecular Collapse

To determine if the particles were in fact unimolecular upon reduction, it was necessary to compare the distribution curves obtained by GPC SLS to the distribution of diameters obtained from the DLS instrument. This was important because our particles collapse in a blend of water and water miscible solvent system eliminating confirmation by GPC and the change in the apparent molecular weights as discussed above. We predicted that each distribution of polymer chains should collapse into a distribution of particles with diameters that could be calculated based on the molecular weight fractions of the polymers. It was assumed that the density of the polymer chains were equal to the bulk density of the polymer ρ_p, 1.2 g/ml. The volume which 1.0 gram of polymer occupies, V_{gram} was calculated below:

$$V_{gram} = \frac{1.0 \; gram \; polymer}{\rho_p} \tag{10}$$

next, the number of particles, P at each weight fraction was determined by using

Avogadro's number N_A, and the number average molecular weight:

$$P = (Wt\ fraction * N_A)/Mn \qquad (11)$$

$$V_{chain} = (\frac{V_{gram}}{P}) \qquad (12)$$

This volume was used in the equation of a sphere to get the diameter of each particle at

each molecular weight.

The diameter of the CUP particles was measured by dynamic light scattering,

which measured the Brownian motion of the particles in water by Doppler shifted laser

light. Information pertaining to the refractive index of the particles and the carrier

solvent and the viscosity of the carrier solvent, η_{solv}, had to be used when setting up the

measurement. Another important consideration was the concentration of the sample in

solution. Before a measurement could be taken, the loading index had been checked by

the instrument, this determined if there was sufficient scattering intensity. As the particle

size got smaller, for example, from 100 nm to 25 nm, to 6 nm, the concentration of

particles in solution had to be increased due to the scattering intensity decreasing, as

shown in Table 5.

A comparison was made from commercially available resins to the concentration

requirements and was found to be accurate until the particle size fell below 20

nanometers. The CUP particles in this research ranged in diameters of 5-9 nanometers,

and it was found that concentrations of approximately 8-10 % solids by weight were

required to obtain an acceptable loading index and as previously discussed the viscosity

of the solution was used instead of that of the solvent.

Table 5. Concentration Requirements[32]

Size (nm)	Concentration(ppm)
220	0.2
100	2
50	16
25	150
12	1200
6	10,000

The five polymers were analyzed by GPC and by DLS. The GPC fractions at

different molecular weights were converted to particle sizes. These calculated diameters,

which assume the density to be the same as the bulk, as does the DLS, were plotted

alongside the DLS data in Figures 7-11. The particle size determined from the molecular

weight produced both average size and distribution which were in very good agreement

with that of DLS.   It should be noted that the resolution of the DLS was less than that of

the GPC.
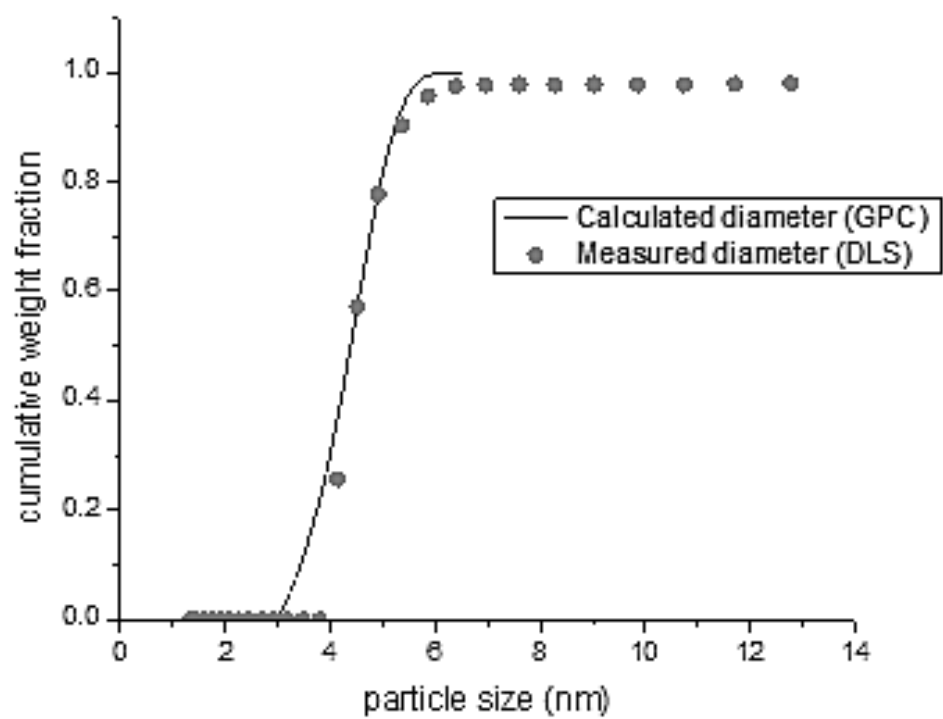
Fig. 7. Polymer 1 distributions
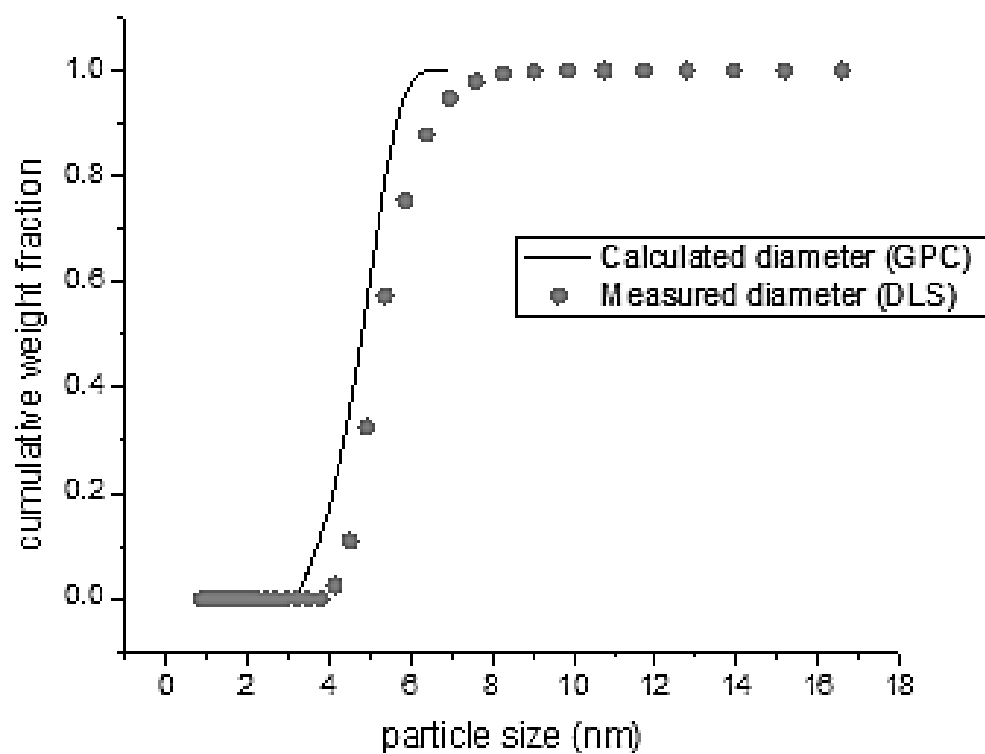
Fig. 8. Polymer 2 distributions
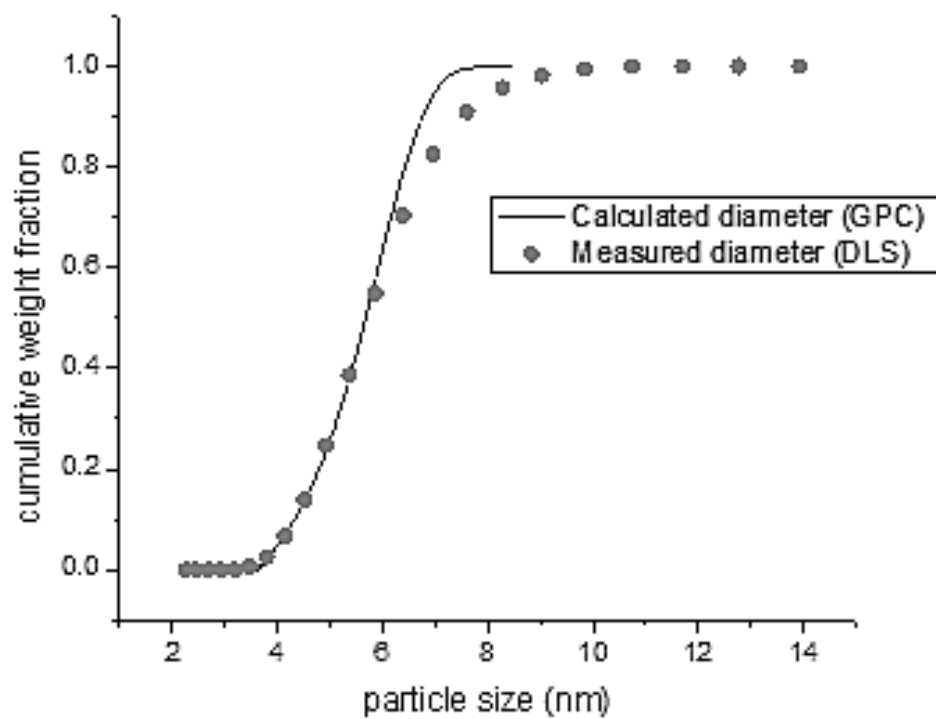
Fig. 9. Polymer 3 distributions
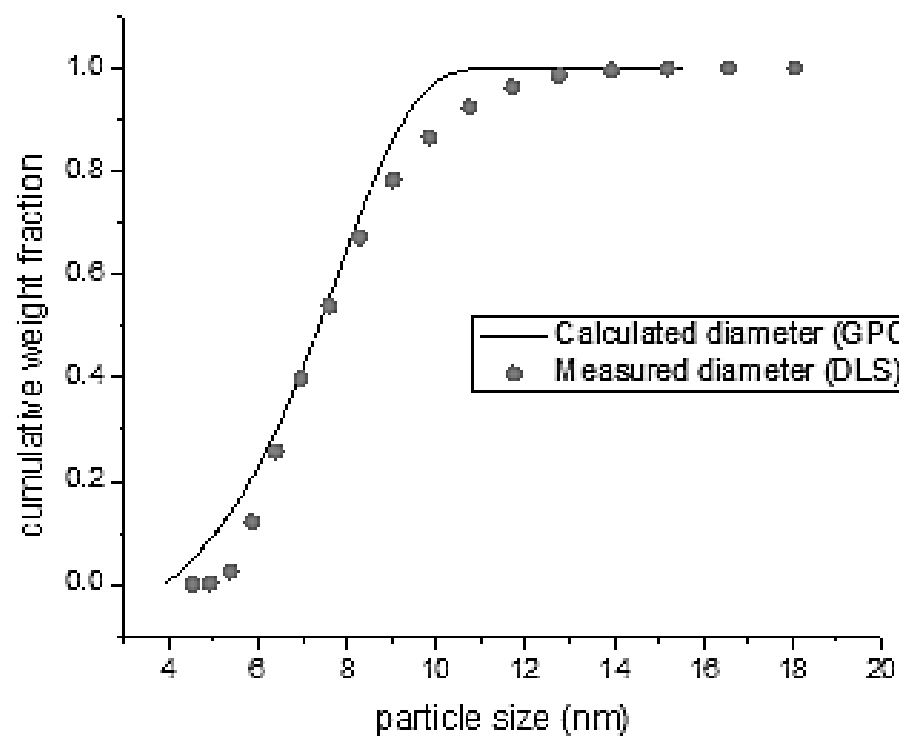
Fig. 10. Polymer 4 distributions
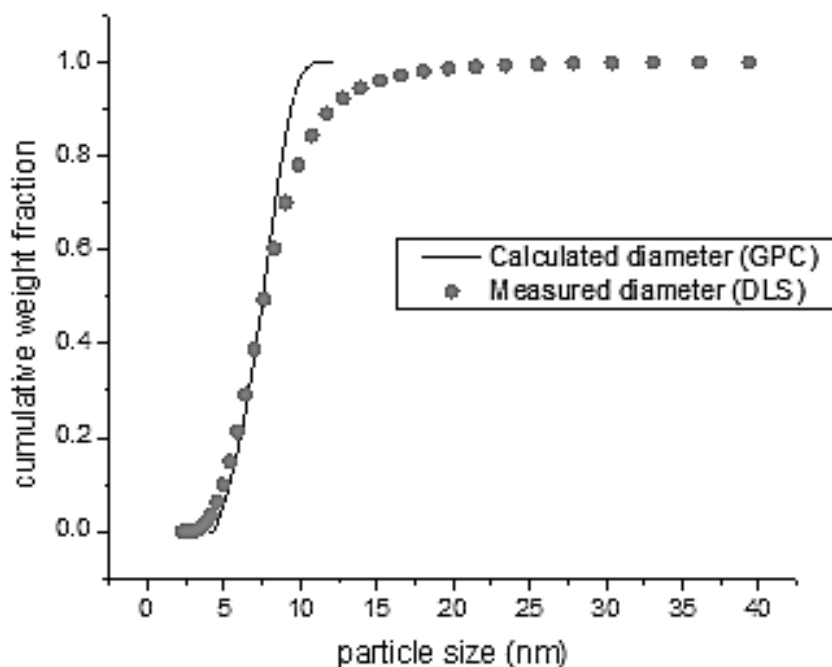
Fig. 11. Polymer 5 distributions

The calculated particle sizes from the GPC results were found to be in good agreement with the diameters measured by DLS. The major difference between the two diameters occurs at the higher particle sizes, which could be a small amount of aggregation or instrumental sensitivity to the higher scattering strength of the larger particles which may over estimate the amount. When the collapse of the polymer chains occurred, it was possible that more than one chain may be entangled, this would not be unexpected. It was not practical to expect 100 % of the polymer chains to be at an exact distance from each other to allow unimolecular collapse; this can be seen by the slight tailing of the measured diameters at higher sizes.

Another factor which influenced the diameter of the measured CUPs was the presence of THF. If the THF was not completely stripped off, it may migrate into the interior of the CUP particle, thus swelling the polymer, giving a diameter which is larger than expected; however, in this research NMR was used to verify complete removal of the THF, less than 0.01%.

4. CONCLUSIONS

A water-reduction process was designed and tested on five polymers of varying molecular weight. All polymers were water-reduced by the method outlined in this research resulting in CUP particles. Correlation between DLS and the absolute Mn distributions obtained from GPC show that the diameter of the CUP particles can be tailored by control of the molecular weight of the polymer. Proof of unimolecular collapse can be seen graphically in that the curves are a close match to each other, meaning that the vast majority of particles did indeed collapse into CUP particles.

The method of water reduction in this research allows the CUP particles to exist in an aqueous medium without the need of a co-solvent, which has been typical of water-reduced resin systems in the coatings industry. By synthesizing various molecular weights, the size of the CUPs can be controlled, allowing the ability to tailor the particles to specific size requirements. Since all that was required was hydrophilic groups and a hydrophobic backbone of the correct ratio, the scope of this type of particle was very broad from coatings to analytical applications. Unlike water soluble resins, these "water insoluble" particles allow applications where no organic solvent can be tolerated.

ACKNOWLEDGEMENTS

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32.   Microtrac Nanotrac 250 particle size analyzer manual

APPENDIX

Figures 12-16 GPC Data for Polymers 1-5

Fig. 12. Polymer 1 GPC Data

RX20   Printed: Thursday, March 15, 2012 10:55:47
C:\Users\Mom's\Desktop\GPC\Cynthia Riddles\2011-12-24_03;14;37_RX20_01.vdt

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)		11.445
Mn - (Daltons)		52,536
Mw - (Daltons)		66,921
Mz - (Daltons)		88,260
Mp - (Daltons)		86,597
Mw / Mn		1.274
Percent Above Mw:	0	0.000
Percent Below Mw:	0	0.000
IV - (dl/g)		0.2020
Rg (Flory-Fox) - (nm)		7.620
Rg - (nm)		No Calc
Wt Fr (Peak)		1.000
Mark-Houwink a		0.608
Mark-Houwink logK		-3.597
Branches		0.000
Branch Freq.		0.000
RI Area - (mvml)		129.53
UV Area - (mvml)		0.00
RALS Area - (mvml)		9.11
LALS Area - (mvml)		5.98
IVDP Area - (mvml)		13.49

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.427	0.000
Sample Recovery (%)	0.000	0.000
dn/dc - (ml/g)	0.0000	0.0833
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	training-0002.vcm
Limits File	011-12-24_03;14;37_RX20_01-training-0002-0001.lim
Date Acquired	Dec 24, 2011 - 03:14:37
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate - (ml/min)	0.500
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00167
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	22.0
OmniSEC Build Number	359

Fig. 13. Polymer 2 GPC Data

RX 21 Printed: Thursday, March 15, 2012 11:33:20
C:\Users\Mom's\Desktop\GPC\Cynthia Riddles\2012-03-01_16;07;06_RX_21_01.vdt

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	11.723
Mn - (Daltons)	62,895
Mw - (Daltons)	87,341
Mz - (Daltons)	120,032
Mp - (Daltons)	118,297
Mw / Mn	1.389
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.1357
Rg (Flory-Fox) - (nm)	7.279
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.514
Mark-Houwink logK	-3.398
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	123.45
UV Area - (mvml)	0.00
RALS Area - (mvml)	8.07
LALS Area - (mvml)	5.72
IVDP Area - (mvml)	11.30

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.924	0.000
Sample Recovery (%)	0.000	0.000
dn/dc - (ml/g)	0.0000	0.0589
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	training-0002.vcm
Limits File	2-03-01_16;07;06_RX_21_01-training-0002-0001.lim
Date Acquired	Mar 01, 2012 - 16:07:06
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate - (ml/min)	0.500
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00167
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	22.0
OmniSEC Build Number	359

Fig. 14. Polymer 3 GPC Data

RX23   Printed: Tuesday, April 03, 2012 12:21:59
C:\Users\Mom's\Desktop\GPC\Minghang Chen\cindy's polymers\2011-12-24_05;47;07_RX23_01.vdt

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)		11.185
Mn - (Daltons)		77,478
Mw - (Daltons)		107,075
Mz - (Daltons)		147,747
Mp - (Daltons)		123,831
Mw / Mn		1.382
Percent Above Mw:	0	0.000
Percent Below Mw:	0	0.000
IV - (dl/g)		0.2521
Rg (Flory-Fox) - (nm)		9.558
Rg - (nm)		No Calc
Wt Fr (Peak)		1.000
Mark-Houwink a		0.585
Mark-Houwink logK		-3.544
Branches		0.000
Branch Freq.		0.000
RI Area - (mvml)		119.70
UV Area - (mvml)		0.00
RALS Area - (mvml)		12.34
LALS Area - (mvml)		8.41
IVDP Area - (mvml)		16.20

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.464	0.000
Sample Recovery (%)	0.000	0.000
dn/dc - (ml/g)	0.0000	0.0750
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	training-0002.vcm
Limits File	)11-12-24_05;47;07_RX23_01-training-0002-0002.lim
Date Acquired	Dec 24, 2011 - 05:47:07
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate - (ml/min)	0.500
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00167
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	22.0
OmniSEC Build Number	359

Fig. 15. Polymer 4 GPC Data

Fig. 16. Polymer 5 GPC Data

Figures 17-18 Submerged and un-submerged water addition during reduction.

Fig. 17. Submerged water addition

Fig. 18. Un-submerged water addition

II.   Use of ^{19}F-NMR T$_2$ Relaxation to Probe the T$_g$ and Core Environment of CUP Particles in Aqueous Media

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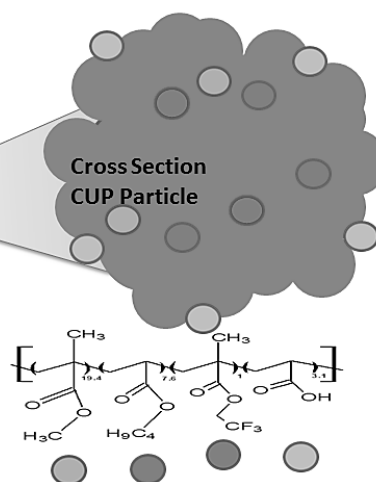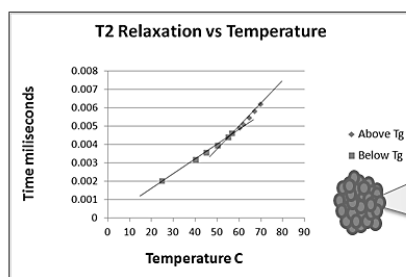
	DSC	Solid State NMR	^{19}F NMR
		Side Chain C	Side Chain F
Tg	57°C	57°C	56°C

ABSTRACT

The interior of Colloidal Unimolecular Polymer (CUP) particles was investigated by using trifluoroethyl methacrylate (TFEMA) as the NMR probe. ^{19}F-NMR T_2 relaxation experiments were utilized as a function of temperature to evaluate the mobility of the trifluoroethyl group. The CUP particles were spheroidal and of 4.6 nm in diameter suspended in water. These particles exhibited a change in the slope of the T_2 rates versus temperature at 56 °C at a point similar to the T_g determined by solid state CP-MASS-TOSS and also the onset of the T_g by DSC. These results indicate that the CF_3 of the TFEMA group was in the solid interior of the CUP particle and behaves like the bulk polymer even though they are in aqueous suspension.

Introduction

Colloidal Unimolecular Polymer, CUP, particles are a new spheroidal single chain macromolecule suspended in water. CUP particles have been shown to be useful as an additive to make latex paint freeze thaw stable [1], as an acid catalyst [2], and as a resin technology. The particles can be crosslinked and are VOC free and are nanoscale unlike latex.[3,4] The synthesis of the CUPs and the water reduction process by which they were formed, has been described in earlier papers.[5,6] Also known as single chain nano particles, the CUPs were formed by a general water reduction process that was performed after the neutralization of ionizable groups along the polymer chains and then slowly subjected to an increasingly poor solvent environment. At a volume ratio of approximately 60% water to 40% THF the polymer-polymer interactions overcame the

polymer-solvent interactions and the polymer chains collapsed into spheroidal particles. The hydrophobic portions of the chains made up the interior domain of the CUP particles, and the hydrophilic groups oriented to the outside in the water phase, similar to the behavior of micelles. Once collapsed, the organic solvent was stripped off resulting in the CUP particle being suspended in VOC-free water. The diameter of the particles was dependent on the molecular weight of the polymer chains, unlike micelles whose diameters are approximately twice the length of the surfactant used. [7]

One of the most important benefits of these CUP particles is the fact that they are VOC and surfactant free. CUPs are suspended in a VOC-free aqueous media. These "water insoluble" particles allow applications where no organic solvent can be tolerated.

The diameter of the CUP particle was easily controlled by the molecular weight of the polymer and calculated by using data obtained through GPC and the density of the bulk polymer. The volume which 1.0 g of polymer occupies, V_g was calculated below:

$$V_{g=\frac{1.0\ g\ polymer}{\rho p}}$$

(1)

Next, the number of particles, P, at each weight fraction was determined by using Avogadro's number N_A, and the number average molecular weight:

$$P = (Wt\ fraction\ *\ N_A)/M_n \tag{2}$$

$$V_{CUP} = (V_g/P) \tag{3}$$

This volume was used in the equation of a sphere to get the diameter of each particle at each molecular weight fraction. Other synthetic polymerization methods such as living

radical polymerization would allow a narrower molecular weight distribution, and in turn result in a narrower distribution of diameters.

The ability to tailor the collapsed particles to specific diameters was one advantage of these nanoparticles. In order to accurately predict the CUP diameters by equations 1-3, the density of the bulk dry polymer was used. Since CUP particles were suspended in aqueous media a determination was needed as to whether the CUPs had the same density even in suspension, as that of the bulk polymer, a dry solid. If both densities are the same, then the Tg of both would also be the same, if different, then the CUPs contain free volume possibly due to trapped water in the interior, or arising from the carboxylate groups being in the interior, and not in the aqueous phase.

Previous work by Mistry [3,4] showed that upon collapse, carboxylate groups of the polymer chains were oriented into the water phase of the CUP particles. The polymers were water reduced and solvent was stripped to produce colloidal unimolecular polymers (CUPs). These particles were typically 3–9 nm in diameter and were also dependent on the molecular weight of the polymers. Ratio of acid groups to monomers was 1:8 and 1:7 similar in the balance of hydrophobic and hydrophilic groups as the polymers used in this research. The CUP solution was then formulated into clear coatings and crosslinked with melamine[3] and aziridine[4] as the crosslinker. These were then cured thermally and compared to commercial latex films. In both instances these crosslinked acrylic CUPs had a distinct advantage of having near-zero volatile organic content, better availability of surface functional groups, and improved water resistance than the commercial latex films. The ability of these particles to be highly crosslinked showed the ability of

carboxylate groups at the surface of the CUPs, but another method was needed to investigate the dynamics of the interior domain.

NMR T_2 relaxation methods have been used to measure changes in the mobility of specific nuclei during experiments.[8-11] These experiments included the formation of micelles and different conformation of polyelectrolytes which tumbled at different rates.

The research group of de Graff [8], focused on AB and BAB block copolymers which were polyethylene glycol (PEG) as A blocks and poly(N-isopropylacrylamide) (PNIPAM) as B blocks in an aqueous environment. Relaxation measurements of both spin-lattice (T_1) and spin-spin (T_2) were used to determine that both star and flower-like micelles were formed by the block copolymers. By measuring with DLS it was found that the radius of the tri-block micelles were smaller than those of the di-block 27 vs 35 nm. The relaxation rates measured for both the star and flower types of micelles, below the cloud point, have little change in both the T_1 and T_2 relaxation times. Above the cloud point there was a small difference in the T_1 relaxation and a very noticeable difference in T_2. This difference was an indication that the motion of the micelles had changed. The T_2 signal from the PEG A blocks showed splits into a fast and slow component showing that the two different motions from the PEG A blocks were occurring. The T_{2fast} component was higher in the tri-block micelle. The authors state that this was the result of the difference in the hydrodynamic radius of the two different micelles formed and relate this to the Stokes-Einstein-DeBye relationship:

$$D_0^r = \frac{K_B T}{8\pi\eta_0} 1/a_T^3 \qquad\qquad (4)$$

If the value of a is smaller, as it was for the tri-block micelles (27 nm versus 35nm for the di-block), the rotational diffusion D was larger. This caused the smaller micelles to have a shorter rotational correlation time which in turn translates into a longer T_2 time. The T_{2slow} for the tri-block micelle was shorter than the T_{2slow} for the di-block. The authors explain this as the relaxation of the distal portions of the PEG groups i.e. they are more flexible leading to fast internal motion. This difference was due to the structure of the flower micelle with the loops rather than the star micelles. The PEG loops have in themselves two spin-spin relaxation time constants, one where the mobility is limited (more internal) and another for the distal (away from the center) portions.

Weiss et al [9] also looked at the relaxation rates of micelles formed by using double thermo responsive di-block copolymers. The two polymers P1 and P2 had the same blocks poly (N -ethyl acrylamide) and (N -propyl acrylamide), however the length of the blocks was varied. For Polymer 1 (PNEAM 94-b-PNPAM 34, P1), and Polymer 2 (PNEAM 133-b -PNPAM 133, P2). These were end capped with trimethylsilyl (TMS) giving a singlet for the TMS. The micelles formed the hydrophilic portion from PNEAM blocks and the hydrophobic core PNPAM. The signal from the TMS moiety on the PNPAM groups broadened to the point that the authors focused solely on the TMS groups on the initial RAFT end of the PNEAM block (TMS$_R$) and the second on the terminal end (TMS$_Z$). The authors also found the T_2 measurements showed a fast and a slow component at all temperatures studied, while all T_1 values consisted of just one component. From this information, it was hypothesized that both star and flower micelles were present in the transition from the lower critical solution temperature and past the cloud point. Signal broadening occurred due to the TMS$_R$ groups forming both star and

flower shape micelle as they were close to the core, and also remaining signals from TMS$_Z$ which show the end group was in the mobile phase like a star shape micelle.

NMR relaxation has also been used to show evidence of the formation of micelle aggregates in aqueous solutions. [10] Evertsson et al studied both T_1 and T_2 relaxation times in three systems. The systems were composed of ethyl(hydroxyethyl)cellulose EHEC, sodium dodecyl sulfate SDS, polyethylene oxide PEO and water in mixtures of EHEC/SDS/water, SDS/water and PEO/SDS/water. In these experiments the ^{1}H NMR relaxation of the methyl protons of the SDS were measured as the concentration of the SDS was slowly increased. For the three systems there was a significant drop in the T_1 times at concentrations that are in agreement with literature values of the critical micelle concentration (CMC) of SDS. The range of time difference was similar in all systems measured. The relaxation time continued to drop slowly as the concentration of SDS was increased.

When measuring the T_2 values of the same systems, a drop in the T_2 time was also seen at the CMC onset of aggregation. The range of time was not similar for all systems like it was for the T_1 measurements. For the EHEC/SDS/water system a more drastic drop in the relaxation times from 0.65 to 0.1 second was observed, where the PEO/SDS/water and the SDS/water were similar. The authors noted that this was likely due to the rigid backbone of the EHEC and a denser mixed polymer micelle. For both relaxation methods, the drop in relaxation times was a clear indication of the formation of aggregates and the slowing of the tumbling of the methyl groups.

Partly fluorinated polyelectrolytes were synthesized by Nurmi et al [11] as possible ^{19}F MRI-detectable nanoparticles. In this paper the authors discussed the problems with

the highly hydrophobic nature of the fluorine atoms which causes aggregation in water and results in a loss of mobility thereby decreasing the signal intensity. For MRI imaging this is a large problem to overcome, and led the authors to synthesize the fluorine containing monomers with charged water soluble monomers. The polymers were statistical and block copolymers of trifluoroethyl methacrylate (TFEMA) and 2-(dimethylamino) ethyl methacrylate (DMAEMA).

The polymer composition, polymer charge density, solution ionic strength and solution pH were varied while both T_1 and T_2 relaxation measurements were taken. By varying these properties, the polymer conformations ranged from extended coil to extended coil intermediate and collapsed globule. The conformations were measured using dynamic light scattering (DLS). The more extended chain conformation resulted in higher T_1 and T_2 times and the collapsed globule the shorter times. The T_1 values ranged from ~310 ms collapsed globule to ~ 520 ms extended coil. The T_2 relaxation time ranged from ~10 ms for the collapsed globule to ~ 150 ms for the extended coil. The large difference in the T_2 relaxation times was similar to what Evertsson's group reported, and was due to the change in mobility causing the most significant variance. In all cases, a decrease in the T_2 relaxation time was attributed to the nuclei becoming more restricted in mobility.

In this research 2, 2, 2-trifluoroethyl methacrylate (TFEMA) was incorporated as a random copolymer with methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA). Tagging this polymer with the TFEMA allowed ^{19}FNMR T_2 relaxation measurements to be made on the reduced CUP particles. Increasing the temperature of the CUP solution should show a slow increase in the T_2 relaxation times, up until the T_g is

reached. At this point, a noticeable increase should be seen as the segmental motion of the polymer is increased allowing the fluorine nuclei to increase mobility. If no noticeable increase is seen this would indicate that the fluorine nuclei were freely spinning even at lower temperatures meaning they resided in the aqueous phase with the carboxylate groups or water plasticizes the CUP interior.

The ability to tailor the size of the CUPs and the placement of specific groups in the interior, or exterior gives more versatility to these particles. The potential use of the CUPs may include drug delivery systems, crosslinking resin technology and possible surfaces for catalysts.

Results And Discussion

Polymerization

The 2,2,2-trifluoroethyl methacrylate (TFEMA), methyl methacrylate (MMA), butyl acrylate (BA) and acrylic acid (AA) were radically copolymerized to produce the ^{19}F tagged polymer.   The TFEMA monomer was randomly incorporated along the polymer chain in the molar ratio shown in **Figure 1**. The ionizable groups on the chain were the acrylic acid monomer. Since CUP formation does not require specific placement of groups along the backbone, use of a random copolymer configuration allows easier synthetic routes than other single chain nanoparticles (SCN) which require more specific polymerization techniques or many synthetic steps.[12-14]
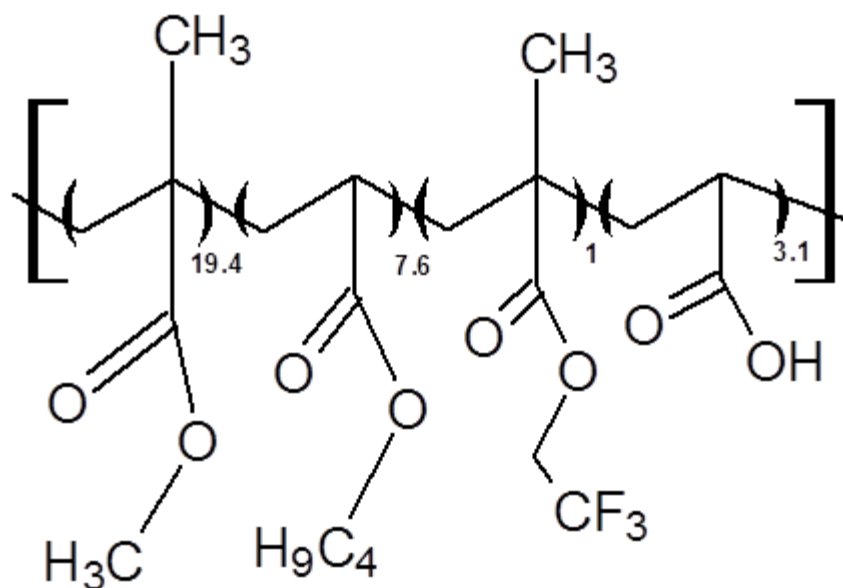
Figure 1. Random Copolymer with Molar Ratios for RX-19

The ratio of non-ionizable monomers to the acrylic acid monomer was approximately a 9:1 ratio which was similar to typical ionic surfactants having approximately 16-22 carbon atoms comprising the hydrophobic portion of the chain to one ionizable group.[15] The ratio of hydrophobic/hydrophilic groups may be adjusted; however, if the number of acid groups is too high the chains will be water soluble, and collapse will not occur, and if too low there will not be enough hydrophilic groups to stabilize the particles. In the latter case, the particles may aggregate or simply precipitate. [16]

Water Reduction to Form CUP

The water reduction process is depicted in **Figure 2.** The polymer chains were dissolved in THF existing in a random coil configuration **I**. Addition of NH4OH neutralized the acid groups **II**. As water was added to the polymer and THF mixture, the

chains took on a more rigid rod conformation causing the solution viscosity to be at a maximum **III.** At the point that polymer chains collapsed into spherical particles, a drop in viscosity was seen **IV**. The same phenomenon has been observed in water reducible resins in the coatings industry.[17] The THF was then stripped off leaving CUP particles **V** suspended in a VOC-free aqueous medium.
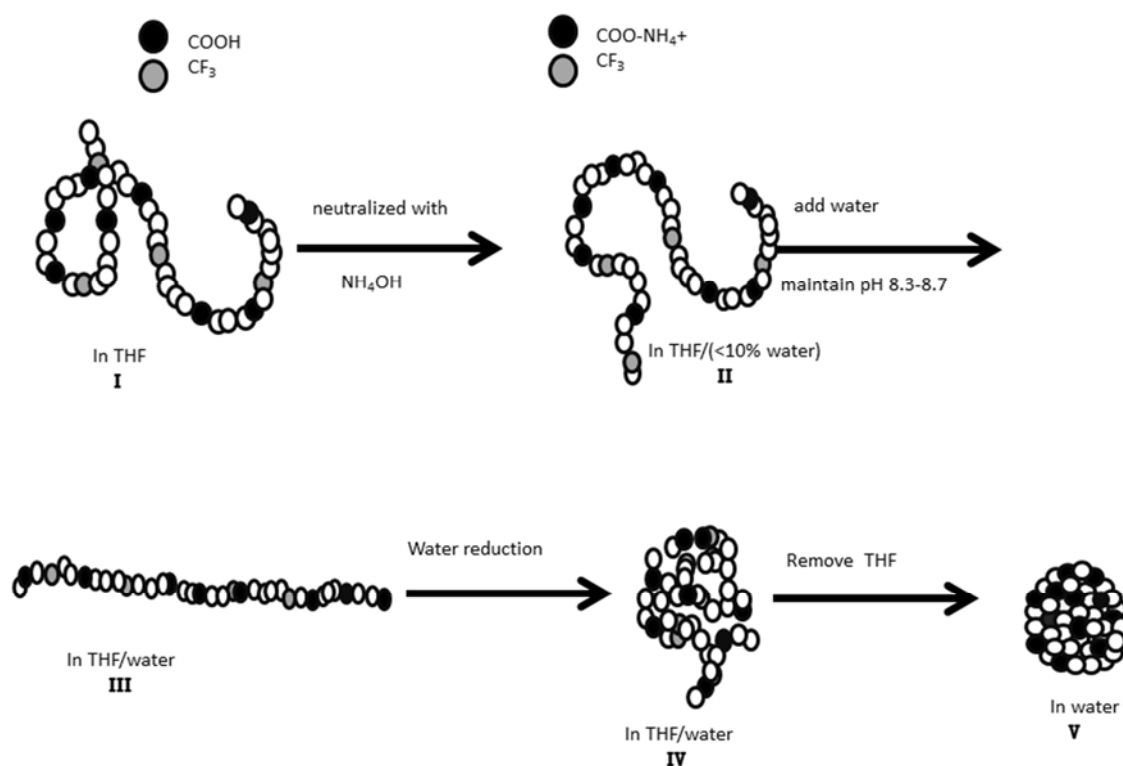
Figure 2. Conformations during Reduction **I** Random coil configuration in THF. **II**. Random coil intimate ion pair**. III**. Rigid rod formation. **IV**. Collapsed coil. **V**. Hard sphere.

In order to show that the polymer chains were in fact unimolecular and spherical after collapse, the distribution curves from the GPC and DLS experiments were graphed. The GPC gave absolute number average molecular weights at points along the distribution curve. From these values, a theoretical diameter was determined by the volume of a sphere equation and polymer density, and then plotted against the DLS values, the two are shown in **Figure 3.** The two distribution curves were a very close match, and show the dependence of the diameter to be directly related to the molecular weight of the polymer and are not aggregated.
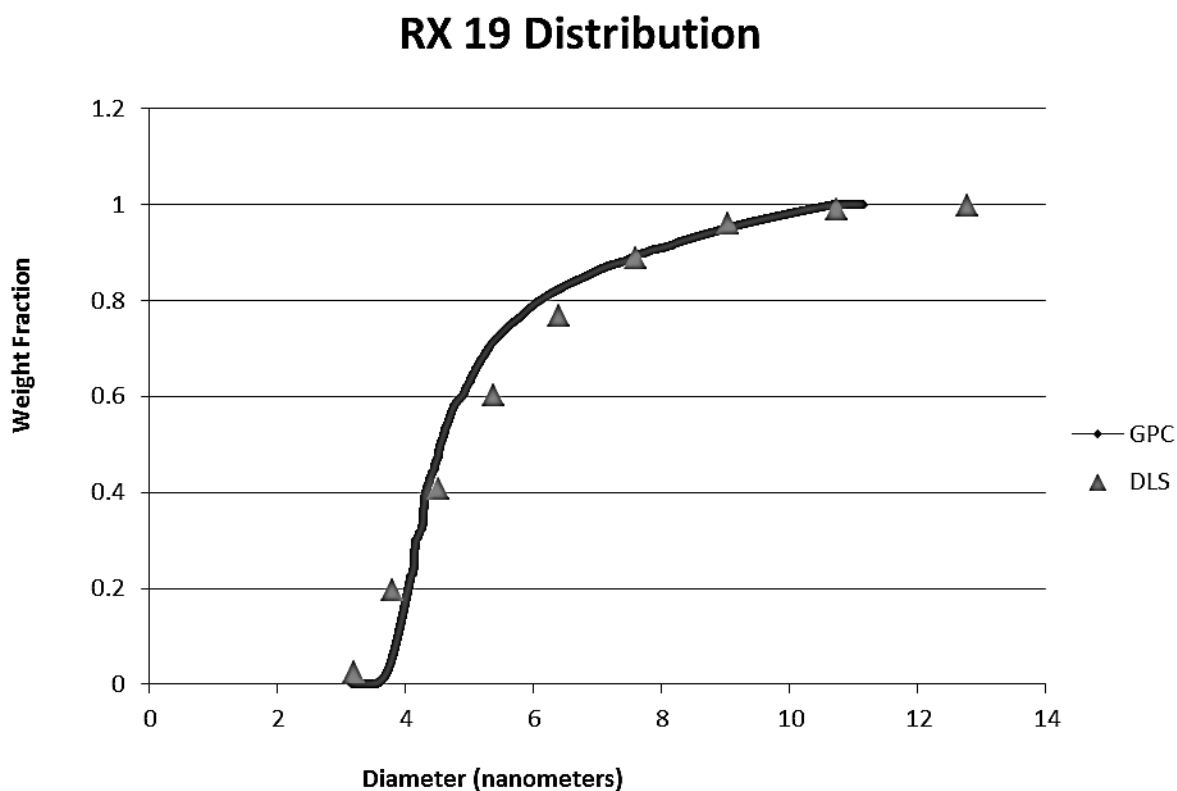
Figure 3.RX-19 Distribution Curves

19FNMR Relaxation Experiments

The ^{19}FNMR spectrum for the collapsed CUP particle at 25°C in D$_2$O is shown in **Figure 4.** The single peak at approximately -75 ppm arising from the three fluorine nuclei of the TFEMA was in agreement with the literature value, also -75 ppm .[18]
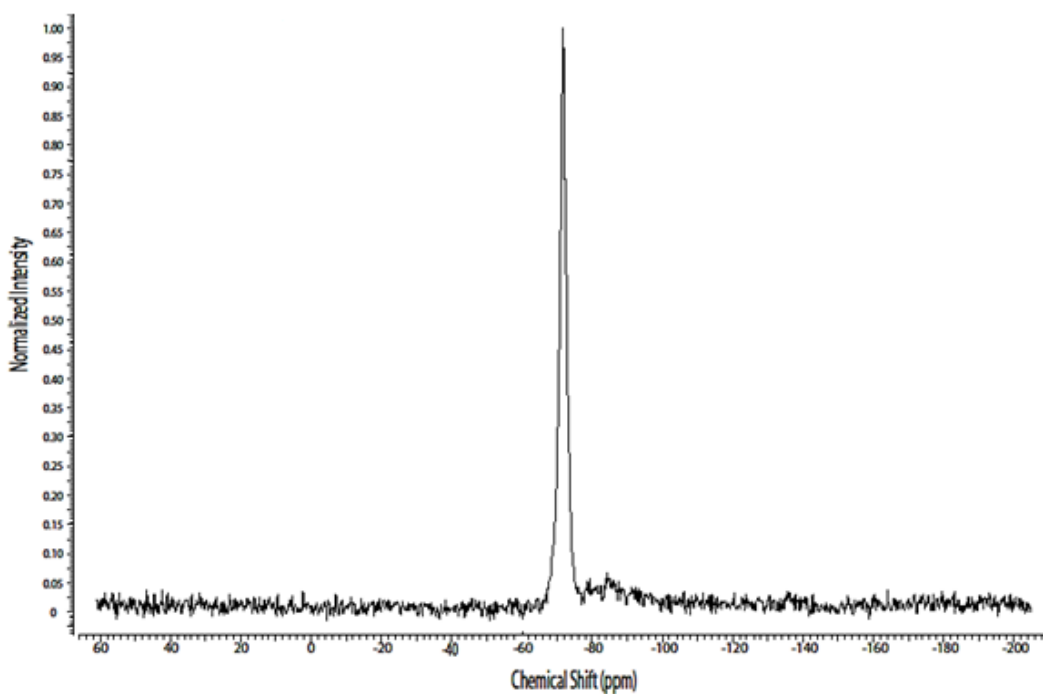
Figure 4. RX-19 CUP particle suspended in D$_2$O at 25C

The T_2 relaxation experiments were performed at temperatures ranging from 25°C to 70°C. This temperature range was selected to be below and above the T$_g$ determined by DSC. The T_2 relaxation times were plotted at each temperature and are shown in **Figure 5.** A distinct deviation from linearity was seen as the temperature approached the T$_g$.

T$_2$ Relaxation vs Temperature
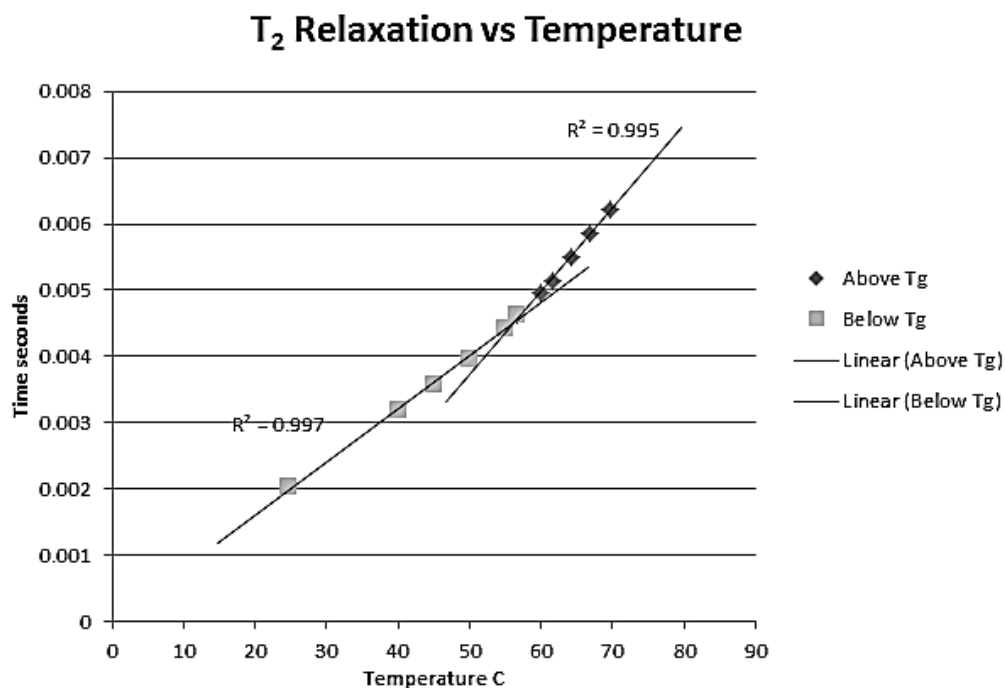
Figure 5. Glass Transition observed for RX-19 from T$_2$ measurements

The data indicate two linear regions, one below, Equation 5 and the other above the T$_g$ region, Equation 6. This intersection point at 56.1°C would imply a change in the mobility of the fluorine atoms at a certain temperature. The *T$_2$* measured for a collapsed globular polymer by Nurmi et al [11] gave a time of 10 ms. This value was above the 2 ms observed here for the CUPs at 25°C. This lower value indicated that the CF$_3$ group was in a more restrictive environment which was anticipated for the polymer below the T$_g$.

$$T_2 = 7.98 \times 10^{-5} \ T + 2.66 \times 10^{-5} \qquad\qquad (5)$$

$$T_2 = 1.25 \times 10^{-4} \ T + 2.52 \times 10^{-3} \qquad\qquad (6)$$

The same deviation of linearity upon heating was seen by Dawib.[19] Dawib measured the glass transition temperature of RX-19 as a bulk solid by solid state NMR

using ^{13}C CP-TOSS NMR peak intensity as a function of temperature.   Solid state NMR

has been used to measure the glass transition temperature of polymers.[20-22] The glass

transition temperature is typically seen at the onset of peak broadening in the NMR

spectrum. As the temperature is raised, segmental relaxation begins to occur causing a

broadening of the peaks of the nuclei being measured. In the work of Dawib, two solid

bulk polymers were used, poly isobutyl methacrylate (PIBMA), **Figure 6** and   the RX-

19 polymer, **Figure 1.**
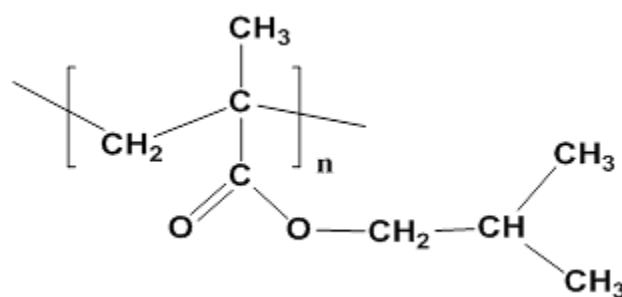
Figure 6. The chemical structure of polymer PIBMA

Both polymers contain methylene carbons and methyl carbons bonded to quaternary

carbons along the polymer backbone. Other similar pendant groups were carbonyl

carbons, (OCH_2), methylene and methyl carbons (CH_2 and CH_3).

The ^{13}C CP-TOSS NMR experiment was carried out at varying temperatures and

peak intensity vs temperature were plotted for each carbon. The graphs showed

analogous linear regions as seen in the current research. The intersection of the two

linear segments was determined to be the onset temperature of molecular motion. For

both polymers the carbons along the backbone and the pendant carbons showed two

different onset temperatures.

The pendant carbon groups were less restricted than the carbons found along the rigid backbone of the polymer chains. As the temperature increased, the pendant groups gained segmental motion before the backbone carbons resulting in a deviation from linearity at a lower temperature.

Dawib evaluated the curves obtained from the MDSC thermogram and noted where the first detectable deviation from the extrapolated baseline occurred. Both the MDSC and CP-TOSS results showed that the side chain movement occurred at 57 °C for the RX-19 bulk polymer. The thermogram obtained by DSC in this research was also evaluated in the same method, and showed deviation from the extrapolated baseline occurred between 55 and 59 °C, and from solution NMR relaxation 56.1°C. Both correspond to the first onset of the T_g observed in DSC at approximately 57°C and confirmed by two different NMR experimental methods. Had the fluorine atoms been in the water phase (on outside of particles) no change in the T_2 slope would have been expected. It should be noted that the onset of deviation in the DSC is not well defined and is therefore less reliable than the NMR methods at detecting initial motion.

Since DSC, CP-TOSS on the bulk material both agree with the ^{19}F NMR of the CUP system, the interior appears to be analogous to that of the bulk material. This implies that the interior is not being plasticized significantly by water and the general model of it being a hard sphere is correct.

Conclusions

A random copolymer containing fluorine atoms was synthesized and water reduced to form CUP particles which were subsequently investigated by ^{19}FNMR T_2

relaxation measurements in solution. The relaxation times as a function of temperature were found to have two linear regions, one above and the other below the onset of the T_g measured by DSC. The intersection of the two linear curves gave an onset T_g of 56.1^{o}C which was in agreement with the extrapolated data from the DSC thermogram for the dry bulk polymer which was 57°C.

The same RX-19 polymer was investigated by Dawib who measured the T_g of the bulk dry polymer by MDSC, and ^{13}C CP-TOSS NMR. The onset T_g for RX-19 from the MDSC was found to be 57°C and 57°C by NMR.

The similarity of the T_g of the CUP to that of the bulk polymer was confirmation that the density and the T_g of RX-19 were the same even though one was the dry bulk polymer and the other, CUP particles suspended in aqueous media.

Experimental Section

Materials

Methyl methacrylate (MMA), butyl acrylate (BA), acrylic acid (AA), 2, 2, 2-trifluoroethyl methacrylate (TFEMA), 2, 2′-azobis (2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. MMA, BA and TFEMA were purified by washing with a 10% (w/w) solution of sodium bicarbonate, followed by rinsing with de-ionized water, and brine. The products were dried over sodium sulfate and filtered. Copper (I) bromide was added to all monomers as an inhibitor, and simple distillation under nitrogen was carried out for MMA and TFEMA. Distillation under reduced pressure was used for AA and BA. The initiator AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received.

Polymerization

Polymerization was by free radical mechanism and carried out in methyl ethyl ketone (MEK), with 1-dodecanethiol as the chain transfer agent, 2-2'-Azoisobutyronitrile (AIBN) as the initiator. To a three-neck flask was added 750 grams of MEK and a magnetic stirring bar. The monomers were then added; MMA 75.68 g (0.76 moles) BA 37.90 g (0.30 mole), AA 8.72 g (0.12 moles) and TFEMA 6.50 g (0.04 moles). Dodecanethiol in the amount of 0.81 g (4 mmole) was added and then AIBN 0.14 g (0.8 mmole). The flask was fitted with a nitrogen line, condenser, and a gas outlet adapter connected to an oil bubbler to allow a positive flow of nitrogen throughout the polymerization. The flask was heated slowly to reflux and allowed to react for 24 hours. The polymer solution was then cooled to room temperature, and precipitated in cold de-ionized water under high shear, then dried under reduced pressure.

The acid number (AN) of the polymer was measured by the titration method given in the ASTM D 974; the method was modified by using potassium hydrogen phthalate (KHP) in place of hydrochloric acid, tetrahydrofuran (THF) in place of ethanol to dissolve the samples and **phenolphthalein in place of methyl orange.** The percent yield and acid number are listed in **Table 1.**

Table 1: Yield and Acid Number

Polymer	Isolated Yield	Measured AN	Calculated AN
		mg KOH/g polymer	
RX 19	75%	60	53

Water Reduction Method

The dried polymer was first dissolved in THF (20% w/w) and allowed to stir overnight. Ammonium hydroxide was added to neutralize the acid groups based upon the acid number. De-ionized water at pH of 8.5 ± 0.2, 2.25 times the weight of THF, was added by a peristaltic pump at the rate of 1.24g/minute. After the water was added, the THF was stripped off in-vacuo. The clear solutions were then filtered with a 0.45 micron filter to remove any extraneous trace contaminants. The typical loss on filtering was less than 0.05% of the solids (w/w).

Instrumental Techniques

^{19}FNMR of poly (methyl methacrylate-ran-butyl acrylate-ran-acrylic acid-ran-trifluoroethyl methacrylate).

The ^{19}FNMR relaxation experiments were carried out using a Varian 400 MHz FT/NMR spectrometer using 5 mm o.d. tube. The dried fluorine tagged polymer was water reduced by the described method.   The experiment solutions were made by mixing 350 micro liters of a 10% (w/w) CUP solution with 400 micro liters of D_2O. For each temperature measured, a new solution was made.

The T_2 relaxation experiments were carried out by the Carr-Purcell-Meiboom-Gill sequence (CPMG) shown in **Figure 7.** The CPMG used an initial 90^0 pulse and when the spin coherences decayed after a time τ, a 180^0 pulse was applied to give a spin echo. The 180^0 pulse was then repeated at various delay times to give a train of echoes.   Each echo was then Fourier transformed, and the integration values were plotted against the delay times to give the T_2 value at each temperature.
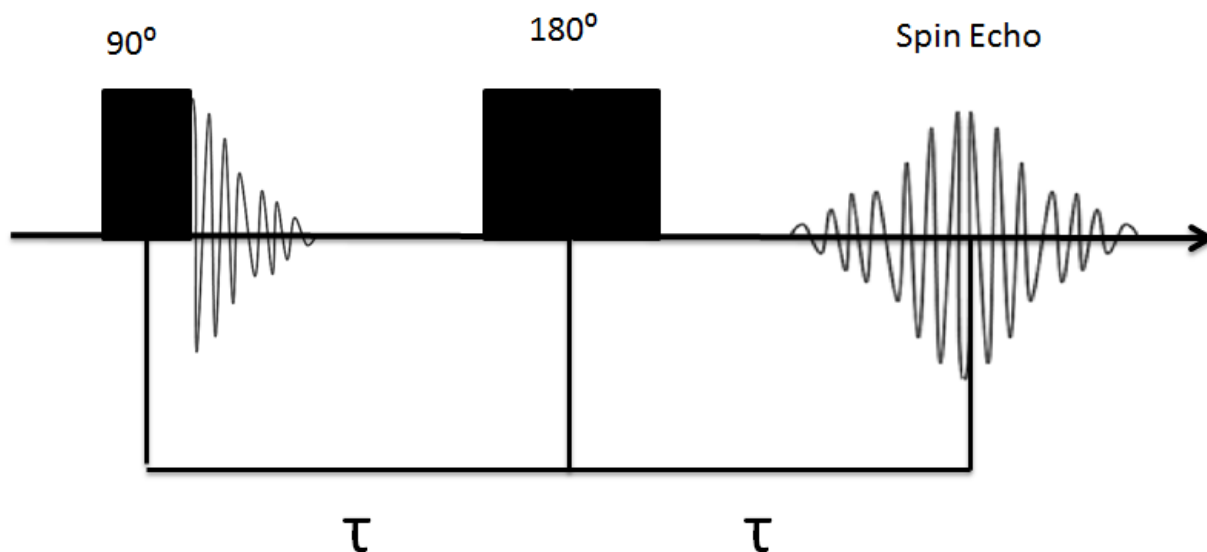
Figure 7. Spin Echo Sequence

¹HNMR of poly (methyl methacrylate-ran-butyl acrylate-ran-acrylic acid-ran-trifluoroethyl methacrylate)

^{1}H NMR (400 MHz, CDCl$_3$): δ 0.85 (3H), 0.95 (2H), 1.03 (2H), 2.00 (3H), 2.16, (3H), 3.59 (3H), 4.35 (2H). Other peaks appearing in the range of 1.15-1.82 were consistent with the polymer backbone methylene.

¹³CNMR poly (methyl methacrylate-ran-butyl acrylate-ran-acrylic acid-ran-trifluoroethyl methacrylate).

^{13}CNMR (400 MHz, CDCl$_3$) δ 176-178 ppm were attributed to the C=O carbons of the following polymers PTFEMA, PBA, PMMA and PAA δ 76.9 OCH$_3$ from PMMA, 77.2 OCH2 from PBA, 77.6 OCH$_2$ PTFEMA 64.8 CF$_3$ from PTFEMA. At 51.9 CH$_2$, 30.52 CH$_2$, 13.84 CH$_3$ butyl group of PBA. Other peaks appearing in the range of δ 15-30 were consistent with the polymer backbone methylene and pendant methyl groups.

Gel Permeation Chromatography.

The absolute number average molecular weight Mn was 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). The polydispersity and Mark-Houwink coefficient of the synthesized polymer along with the Mn are listed in **Table 2.**

Table 2: Molecular weight, polydispersity and Mark Houwink data.

Polymer	Mn SLS (kg/mol)	DLS (nm)	Polydispersity	Mark Houwink log K	a
RX 19	26	4.61	1.71	-3.69	0.64

Particle Size Analysis

The particle size distribution of the CUP particles 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. The CUP sample was 20% (w/w) with an accurate viscosity taken by Ubbelohde viscometer method ASTM D 446-07. The solution viscosity instead of the solvent was utilized for particle size analysis based upon prior work[5] and was used in the Stokes-Einstein Equation (7) by the DLS instrument.

$$D = K_B T / 6\pi\eta r \tag{7}$$

Glass Transition Temperature

Glass transition temperature (Tg) of the synthesized polymers was obtained on a DSC Q2000 from TA Instruments- Waters LLC. Measurements were conducted in

accordance with ASTM standard E1356-08. The modulated DSC (MDSC) method was

applied by heating samples of mass 5-20 mg in premium aluminum hermetic pans DSC#

84010 & 84011from DSC Consumables, Inc. at a heating rate of 2 °C /min over the

temperature range of 0°C to 100°C. The modulated amplitude was ±1°C with a period of

60 s. The temperature of first deviation was the point of first detectable deviation from

the extrapolated baseline prior to the transition and the midpoint temperature was the

point on the thermal curve corresponding to 1⁄2 the heat flow difference between the

extrapolated onset and extrapolated end. The synthesized polymer RX-19 revealed a Tg

value, 68°C, and the first deviation temperature occurred approximately at 57°C+/- 2°C.

The DSC thermogram is shown in **Figure 8.**
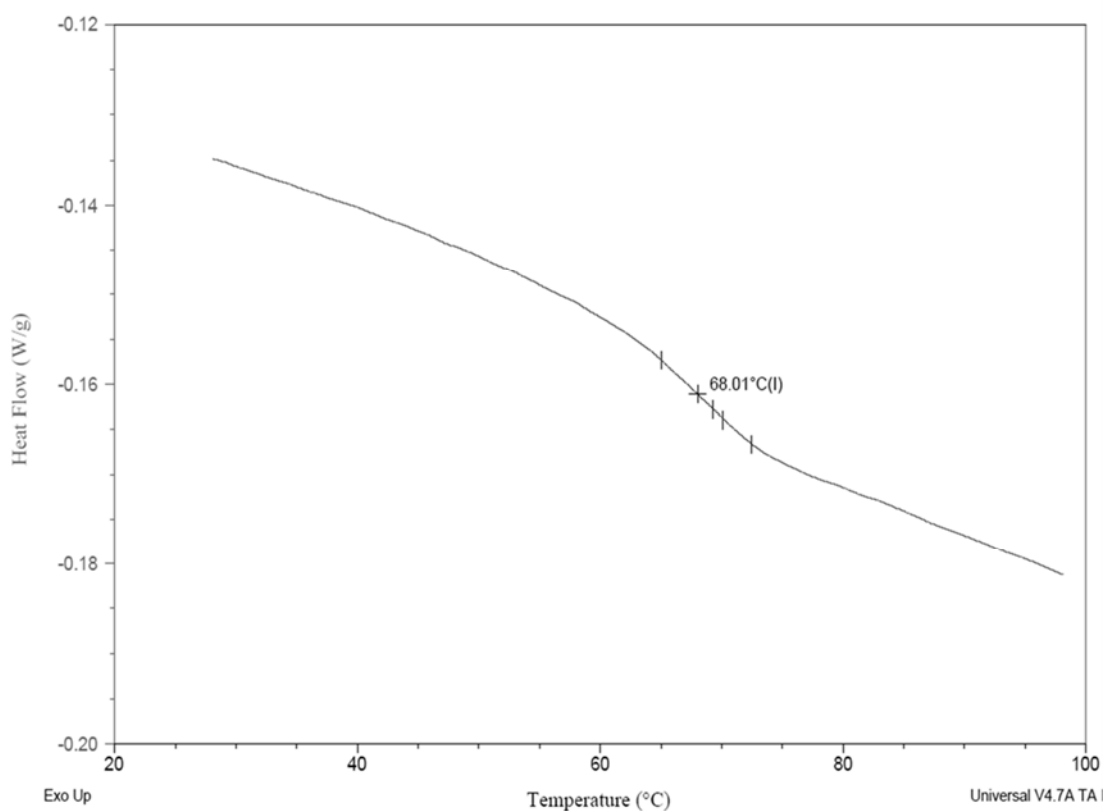
Figure 8. Glass Transition of RX-19 Bulk Polymer by DSC

Acknowledgments

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APPENDIX

Figure 1 RX-19 ^{1}HNMR

Figure 2 RX-19 ^{13}CNMR

Figure 3 RX-19 CUP suspended in D2O

 Figure 4 RX-19 GPC data

Figure 5 RX-19 particle size data

FIGURE 1 RX-19 ^{1}HNMR

FIGURE 2 RX-19 ^{13}CNMR

This report was created by ACD/NMR Processor Academic Edition. For more information go to www.acdlabs.com/nmrproc/

2/25/215 6:43:40 PM

Acquisition Time (sec)	0.0102	Comment	STANDARD 1H OBSERVE		Date	Dec 3, 2011
Date Stamp	Dec 3, 2011	File Name	G:\NMR FILES\F19_25degC-120311.fid\fid		Frequency (MHz)	376.15
Nucleus	19F	Number of Transients	256	Original Points Count	1024	Points Count	1024
Pulse Sequence	s2pul	Receiver Gain	50.00	Solvent	DEUTERIUM OXIDE		
Spectrum Offset (Hz)	-27060.7031	Spectrum Type	STANDARD	Sweep Width (Hz)	100000.00	Temperature (degree C)	25.000

F19_25degC-120311.esp VerticalScaleFactor = 1

FIGURE 3 RX-19 CUP suspended in D2O

RX19   Printed: Thursday, March 22, 2012 11:10:14
C:\Users\Mom's\Desktop\GPC\Minghang Chen\cindy's polymers\2011-12-24_01;58;23_RX19_01.vdt

IV - DP

RALS
LALS

12.06

RI

Detector Response (mV)

Retention Volume (ml)

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	12.060
Mn - (Daltons)	25,962
Mw - (Daltons)	44,486
Mz - (Daltons)	62,773
Mp - (Daltons)	42,362
Mw / Mn	1.713
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.1922
Rg (Flory-Fox) - (nm)	6.365
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.639
Mark-Houwink logK	-3.689
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	119.36
UV Area - (mvml)	0.00
RALS Area - (mvml)	4.85
LALS Area - (mvml)	3.21
IVDP Area - (mvml)	13.51

Sample Parameters

Sample Parameters	Input	Calculated
Sample Conc - (mg/ml)	1.596	0.000
Sample Recovery (%)	0.000	0.000
dn/dc - (ml/g)	0.0000	0.0686
dA/dc - (ml/g)	1.0000	0.0000

Annotation	
Method File	training-0002.vcm
Limits File	)11-12-24_01;58;23_RX19_01-training-0002-0001.lim
Date Acquired	Dec 24, 2011 - 01:58:23
Solvent	THF
Acquisition Operator	admin : Administrator
Calculation Operator	admin : Administrator
Column Set	GMHxl
System	System 1
Flow Rate - (ml/min)	0.500
Inj Volume - (ul)	100.0
Volume Increment - (ml)	0.00167
Detector Temp. - (deg C)	22.0
Column Temp. - (deg C)	22.0
OmniSEC Build Number	359

Log Molecular Weight vs. Retention Volume

WF / dLog M vs. Log Molecular Weight

Mn   Mw Mz

FIGURE 4 RX-19 GPC data

FIGURE 5 RX-19 particle size data

SECTION

2. COUNTER ION AFFECT OF GROUP 1 HYDROXIDES

2.1. INTRODUCTION

One drawback of the CUP particles being ionized with NH_4OH was that if the CUPs were allowed to dry, they would not be able to be re-dissolved due to evaporation of the ammonium ion. Ideally, if the CUPs were to be marketed for the coatings industry, being in powder form would be beneficial. This would allow the customer to have the ability of controlling concentration of CUP solution, and smaller storage needs. Another benefit is the lack of a need for fungicide and biocide used until the CUPs are re-dissolved. For this reason, investigation into alternative bases for the ionization process was necessary.

During initial water reduction trials by others in this research group, it was discovered that de-ionized water must be used rather that tap water. When tap water was used, a coagulum formed and prevented successful collapse of the CUPs. To determine if calcium was the problem, a water reduction was done using water with a small amount of $CaOH_2$ (20ppm). The CUP solution was cloudy and coagulum was present as shown in Figure 1.

The backbone of the polymer chains consist of COO^- and calcium is bivalent thus allowing two polymer chains to become connected to calcium cations. This same problem would be seen using magnesium or any other multi-valent species during the reduction process.

.
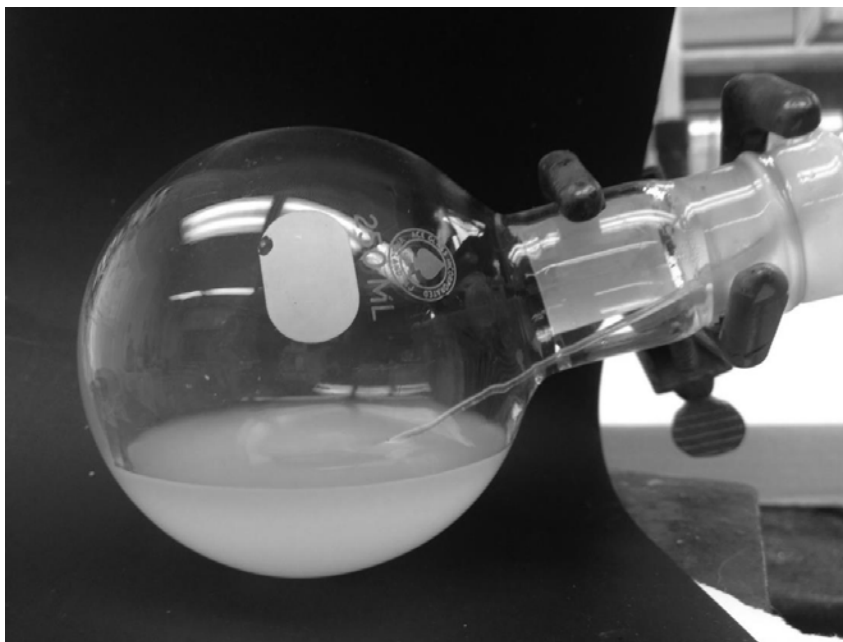
Figure 1. Calcium present at 20ppm

To prevent any coagulum from occurring Group 1 mono valent metals were selected. The metal hydroxides of lithium, sodium and potassium were selected to ensure the CUP solutions retained purity. The hydroxides were dissolved in de-ionized water and the Molarity was measured for each. These bases were then used to neutralize the polymer RX24 and were then water reduced according to the method described in the publications in this dissertation.

Particle size was measured for all three CUP solutions, and then the solutions were roto allowed to dry then crushed into a powder. The powders were re-dissolved de-ionized water and then particle size was measured again. The particle size of the re-dissolved CUPs was compared to the original CUP solutions.

2.2. EXPERIMENTAL

2.2.1 Materials. Methyl methacrylate (MMA), methacrylic acid (MAA), 2,2′-azobis(2-methylpropionitrile) (AIBN), and 1-dodecanethiol were purchased from Aldrich. MMA was purified by washing with a 10% (w/w) solution of sodium bicarbonate, followed by rinsing with de-ionized water, and brine. The product was dried over sodium sulfate and filtered. Copper (I) bromide was added to the MMA as an inhibitor, and simple distillation under nitrogen was carried out. MAA was purified by distillation with copper (I) bromide under reduced pressure. AIBN was re-crystallized from methanol, and 1-dodecanethiol was used as received. Deionized water was used for all experiments.

2.2.2 Polymerization. Polymerization was by free radical mechanism and carried out in methyl ethyl ketone (MEK), with 1-dodecanethiol as the chain transfer agent, 2-2'-Azoisobutyronitrile (AIBN) as the initiator. The reaction was carried out under nitrogen at the reflux temperature if MEK for 36 hours. The solution was then cooled and precipitated in cold de-ionized water under shear. The polymer was then dried reduced pressure.

2.2.3 Gel Permeation Chromatography. The absolute molecular weight of the copolymers was measured using gel permeation chromatography by using a Viscotek model 305 instrument manufactured by Malvern Corp. The flow rate of THF was 0.5 mL/min, and the injection volume was 100 μL. The GPC was equipped with refractive index detector, low and right angle light scattering detector, and intrinsic viscosity detector, thus yielding absolute molecular weight.

2.2.4 Acid Number. Acid number (AN) was 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.

2.2.5 Water Reduction. Polymers were dissolved in THF (10% w/w) and stirred overnight. Sodium hydroxide was added to neutralize the acid groups according to the acid number. To the solution was added an equal amount of water (pH = 8.5−9 adjusted by GROUP1OH) to THF via a peristaltic pump at a rate of 1.24g/min, and the pH of solution was maintained between 8.5 and 9. THF was then stripped in vacuo. Solutions were then filtered through 0.45 μm Millipore membrane to remove any foreign materials which were typically measured to be less than 0.05% by weight.

2.3. RESULTS AND DISCUSSION

2.3.1 Water Reduction. To ensure complete ionization of the polymer chains, a pH of 8.5 is needed. Deionized water was boiled for one hour to remove any dissolved CO_2, then solutions were made beginning with a 1M solution of LiOH, NaOH, and KOH. The Molarity was determined by titration method standardized with KHP. Further dilutions were then made to achieve 0.1 Molar solutions.

These solutions were then used during the water reduction process. The pH was monitored during the reduction process, to ensure the solutions remained alkaline during the process.

2.3.2 Particle Size Measurements. After the water reduction process, all solutions were then filtered with a 0.45 micron filter to remove any extraneous trace contaminants.

Particle size measurements were taken on all three solutions, are shown below in Figures 2-4.
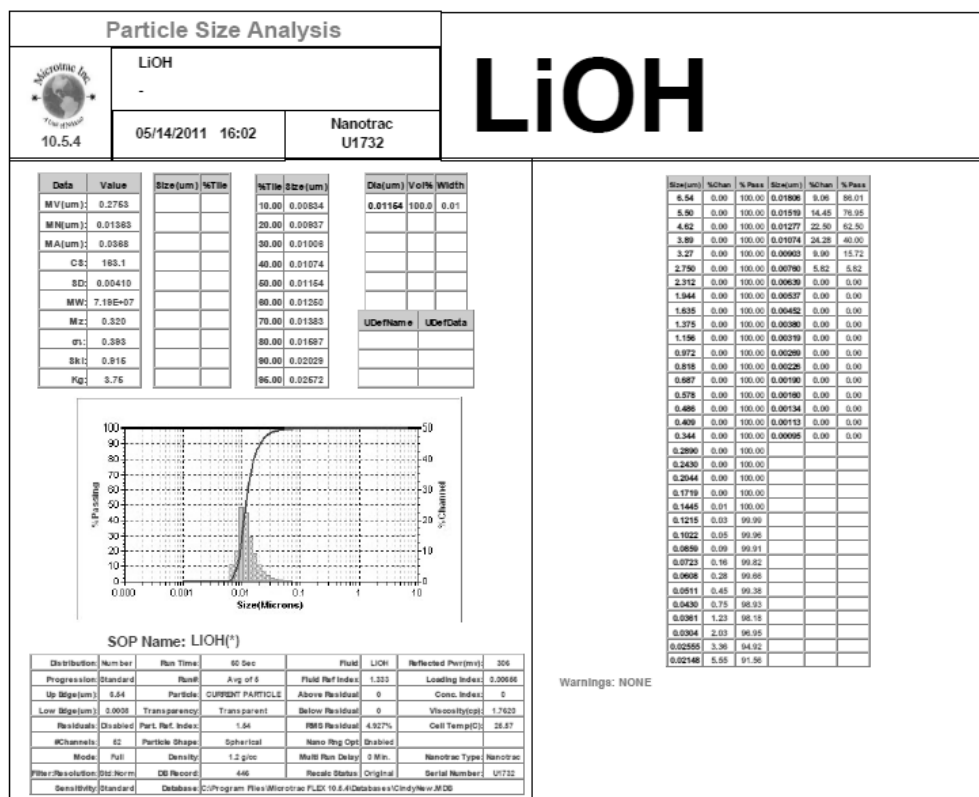
Figure 2. Particle Size Reduced With LiOH

The water reduced solutions were put into a small Erlenmeyer flask with ground glass top and water was stripped off in vacuo until gelled. The gels were then allowed to dry completely. After the drying process, the polymers were crushed into a powder, and de-ionized water was added back to the flasks. The re-dissolved solutions are shown in Figures 5-7.

The solutions were then put into vials and the particle sizes were measured a second time and are shown in Figures 8-10.
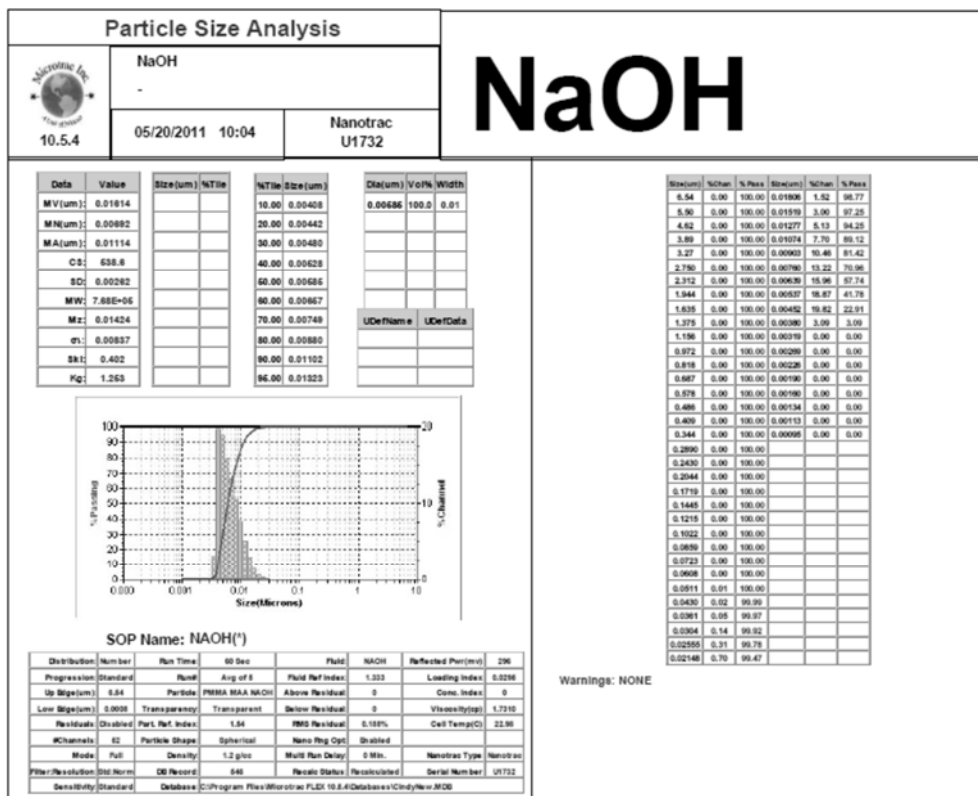
Figure 3. Particle Size Reduced With NaOH

Of the three different counter ions, the CUP containing potassium counter ion showed a better ability to be dried and re-dissolved. The sample showed more clarity than the sodium and lithium.

The lithium showed the presence of coagulum and during the water reduction process required addition base to be added due to a drift in the pH.

Lithium is the smallest cation of the group of bases used, and is therefore more 'hard' than the other two. The $Li^{+-}OH$ bond is held tighter. For KOH the K^+ atom is larger than the other two, and ionizes more readily. The CUP that was neutralized with LiOH also

was the most unstable during the water reduction process requiring multiple additions of

LiOH to the solution to maintain alkalinity.
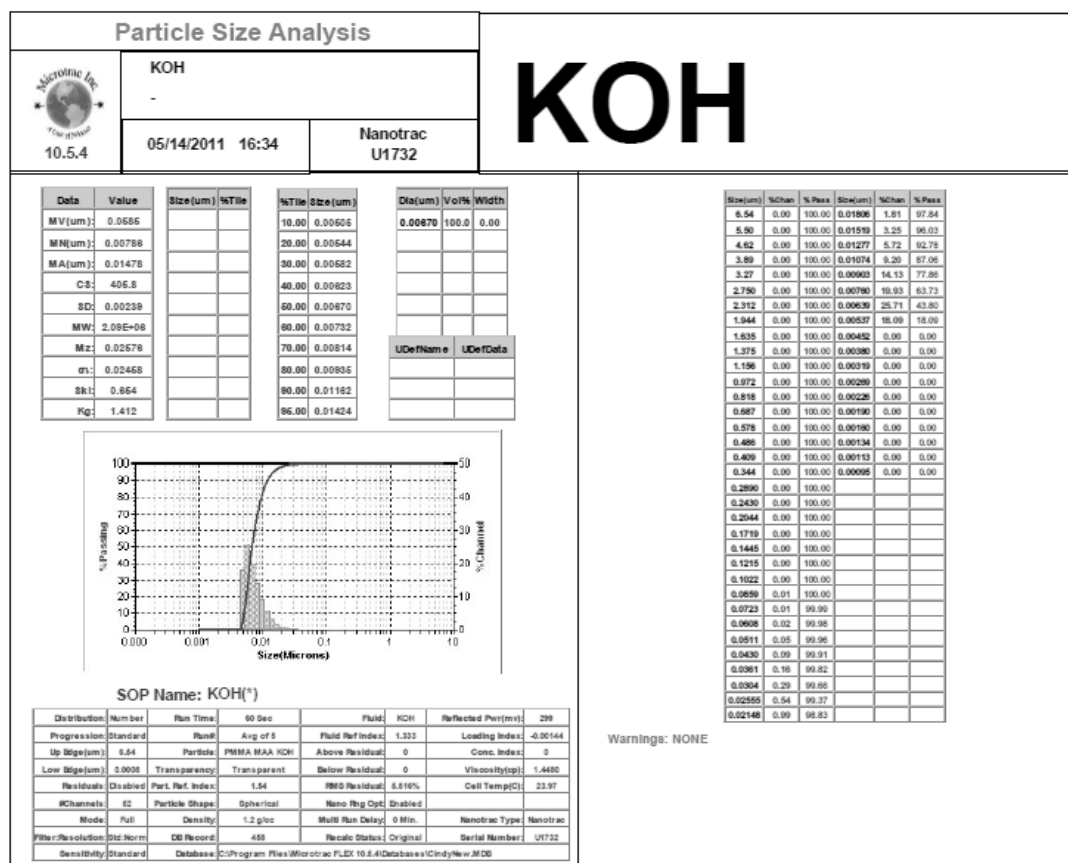
Figure 4. Particle Size Reduced With KOH

2.3.3 Conclusions. The ability of the CUPs to be dried and re-dissolved while

maintaining their integrity was an important discovery. If the CUPs were to be scaled up

in a production environment, being in a powder form would be ideal. The dried CUPs

are more lightweight and take up less volume than the suspended form. Another

consideration is the inherent nature of water to allow organisms to grow.

Figure 5. Re-dissolved CUP with Li
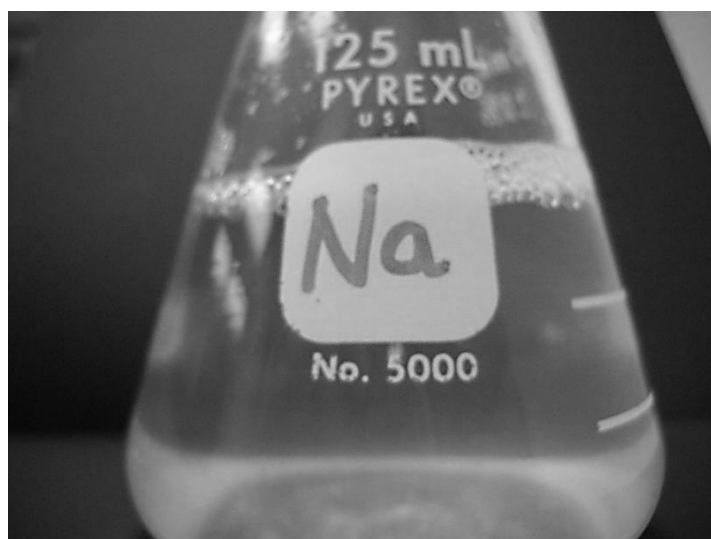
Figure 6. Re-dissolved CUP with Na

3. CONCLUSIONS

The CUP particles described in this research are an important new technology for the coatings industry, and polymer science. The polymers are synthesized by free radical mechanism and the diameters of the collapsed particles can be controlled by the molecular weight.

In the coatings industry, waterborne resins, colorant dispersions and additives typically have a biocide package added to them. Biocides are heavily regulated and the levels vary from region to region globally.
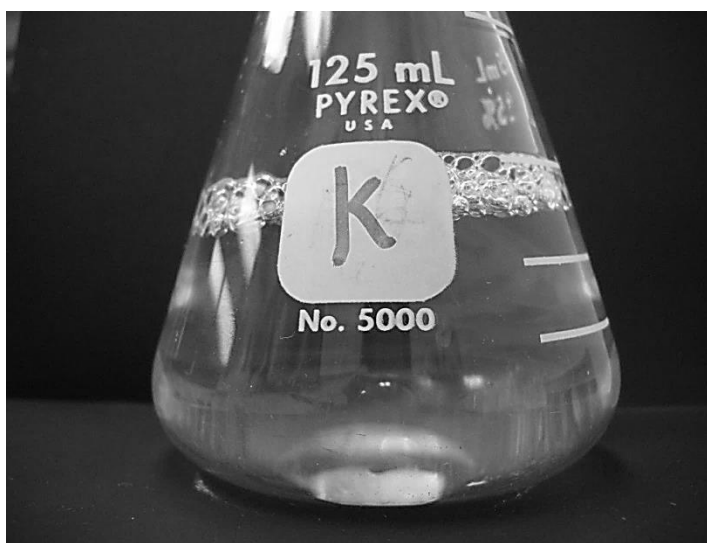
Figure 7. Re-dissolved CUP with K

Two very significant discoveries were made, first that the density of the bulk dry polymer was the same as that of the CUPs suspended in aqueous media. This was shown through DSC and NMR on both the dry polymer and the CUP solutions. Secondly, evidence of the behavior of the CUPs to be similar to micelles was found. The

ability of the CUPs to be crosslinked with nucleophilic species showed that the reactive

carboxylate groups were oriented in the water phase, and through ^{19}FNMR relaxation it

was shown that the hydrophobic groups resided in the particle interior.
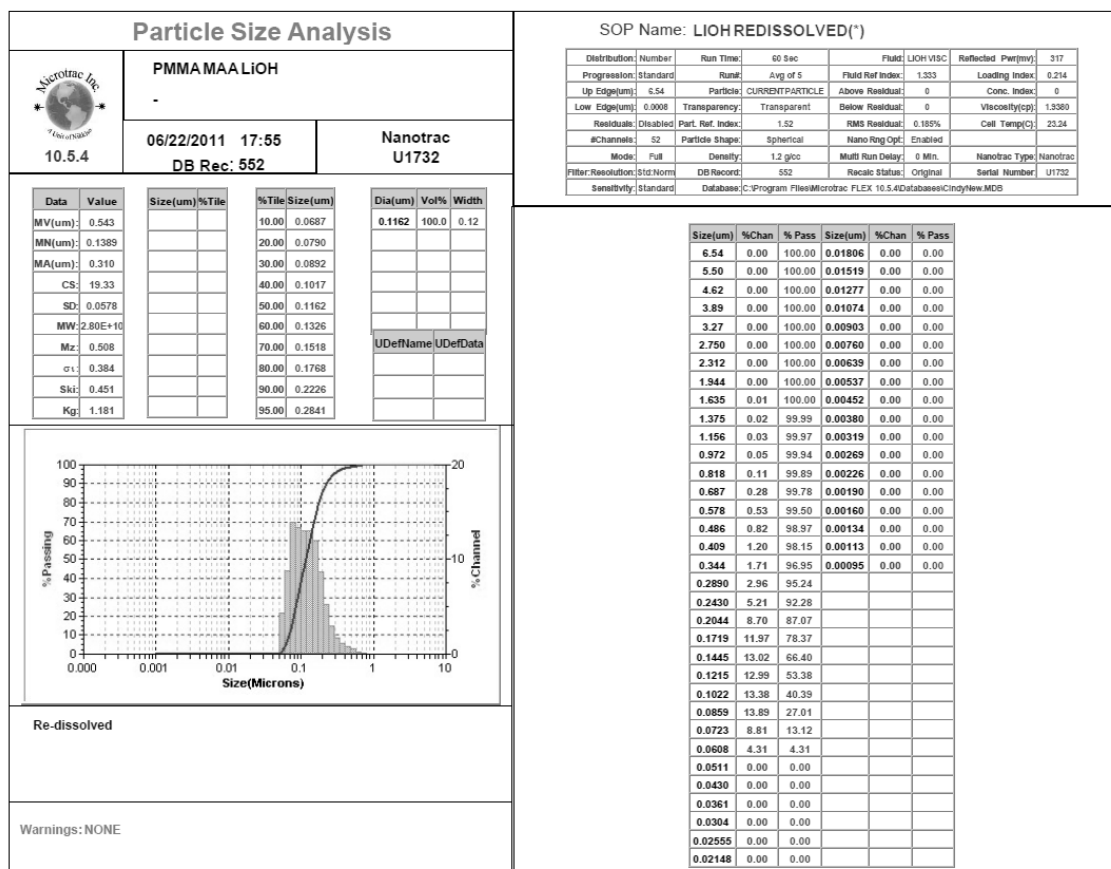
Figure 8. Particle Size Re-dissolved LiOH

These findings will allow more diversity in synthesizing CUPs for more specific

purposes. The carboxylate groups give more functionality to the surface allowing further

reactions to occur, or a hydrophobic moiety can be safely kept in the interior of the

particle.

On a commercial scale, the CUPs could be synthesized and sold as powders, while still maintaining a low particle size when dissolved. The benefit of powdered CUPs vs in solution is that the powder is more lightweight and easier to store. The solutions only have a finite time before organisms begin grow in the water requiring biocides to be added.

Particle Size Analysis

Microtrac Inc.

PMMA MAA NaOH

-

06/22/2011 18:08
DB Rec: 558

Nanotrac U1732

10.5.4

Data	Value
MV(um):	0.02553
MN(um):	0.01032
MA(um):	0.01188
CS:	505.8
SD:	0.00211
MW:	8.08E+05
Mz:	0.01251
ci:	0.00389
Skt:	0.376
Kg:	1.038

%Tile	Size(um)
10.00	0.00766
20.00	0.00831
30.00	0.00866
40.00	0.00934
50.00	0.00981
60.00	0.01031
70.00	0.01092
80.00	0.01180
90.00	0.01336
95.00	0.01518

Dia(um)	Vol%	Width
0.00981	100.0	0.00

UDefName UDefData

Re-dissolved

Warnings: NONE

SOP Name: NAOH REDISSOLVED(*)

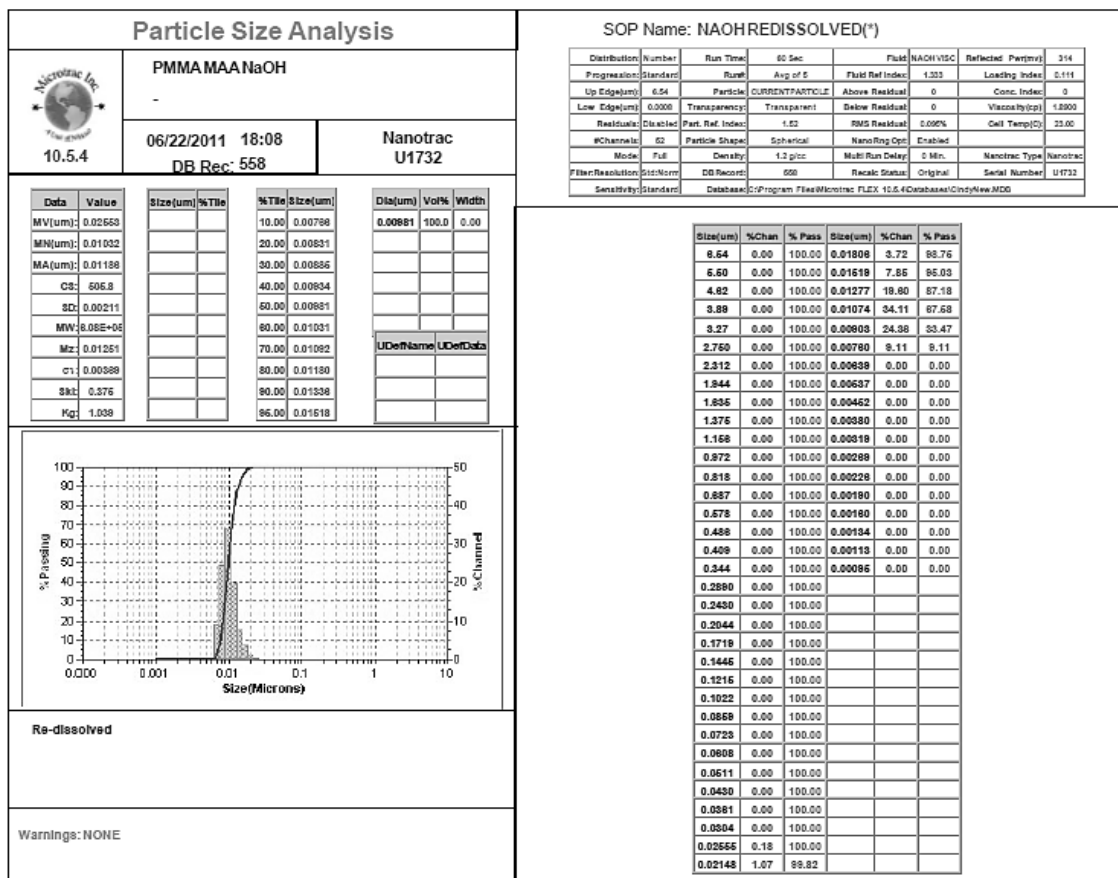|							
Distribution:	Number	Run Time:	60 Sec	Fluid:	NAOH VISC	Reflected Pwr(mv):	314
Progression:	Standard	Run#:	Avg of 5	Fluid Ref Index:	1.333	Loading Index:	0.111
Up Edge(um):	6.54	Particle:	CURRENTPARTICLE	Above Residual:	0	Conc. Index:	0
Low Edge(um):	0.0009	Transparency:	Transparent	Below Residual:	0	Viscosity(cp):	1.8900
Residuals:	Disabled	Part. Ref. Index:	1.52	RMS Residual:	0.096%	Cell Temp(C):	23.00
#Channels:	52	Particle Shape:	Spherical	NanoRing Opt:	Enabled		
Mode:	Full	Density:	1.2 g/cc	Multi Run Delay:	0 Min.	Nanotrac Type:	Nanotrac
Filter Resolution:	Std:Norm	DB Record:	559	Recalc Status:	Original	Serial Number:	U1732
Sensitivity:	Standard	Database:	C:\Program Files\Microtrac FLEX 10.5.4\Databases\CindyNew.MDB				

Size(um)	%Chan	% Pass	Size(um)	%Chan	% Pass
6.54	0.00	100.00	0.01808	3.72	88.76
5.50	0.00	100.00	0.01519	7.85	95.03
4.62	0.00	100.00	0.01277	18.60	87.18
3.89	0.00	100.00	0.01074	34.11	87.58
3.27	0.00	100.00	0.00903	24.38	33.47
2.750	0.00	100.00	0.00760	9.11	9.11
2.312	0.00	100.00	0.00639	0.00	0.00
1.944	0.00	100.00	0.00537	0.00	0.00
1.635	0.00	100.00	0.00452	0.00	0.00
1.375	0.00	100.00	0.00380	0.00	0.00
1.158	0.00	100.00	0.00319	0.00	0.00
0.972	0.00	100.00	0.00289	0.00	0.00
0.818	0.00	100.00	0.00226	0.00	0.00
0.687	0.00	100.00	0.00190	0.00	0.00
0.578	0.00	100.00	0.00160	0.00	0.00
0.486	0.00	100.00	0.00134	0.00	0.00
0.409	0.00	100.00	0.00113	0.00	0.00
0.344	0.00	100.00	0.00095	0.00	0.00
0.2890	0.00	100.00			
0.2430	0.00	100.00			
0.2044	0.00	100.00			
0.1718	0.00	100.00			
0.1445	0.00	100.00			
0.1215	0.00	100.00			
0.1022	0.00	100.00			
0.0859	0.00	100.00			
0.0723	0.00	100.00			
0.0608	0.00	100.00			
0.0511	0.00	100.00			
0.0430	0.00	100.00			
0.0361	0.00	100.00			
0.0304	0.00	100.00			
0.02555	0.18	100.00			
0.02148	1.07	99.82			

Figure 9. Particle Size Re-dissolved NaOH

Particle Size Analysis

PMMA MAA KOH

-

06/23/2011 12:30
DB Rec: 590

Nanotrac
U1732

10.5.4

Re-dissolved
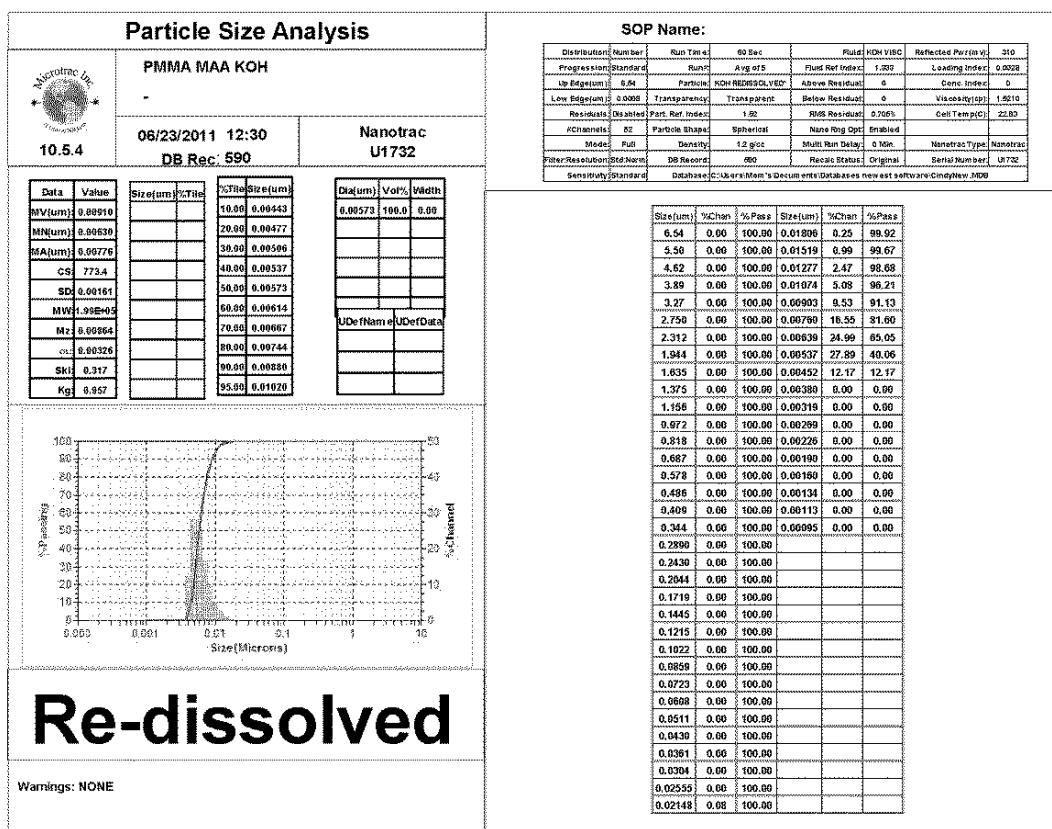
Warnings: NONE

SOP Name:

Figure 10. Particle Size Re-dissolved KOH

REFERENCE

1. Pearson, R. *J. Chem. Educ.* **45** (9), 1968, pgs. 581-587.

VITA

Cynthia Jeannette Riddles was born May 17, 1965 in Toledo Ohio. Cynthia began her college education as a single parent of two children in 1999 and obtained her Bachelor's degree in Chemistry in May of 2005 from Southwest Baptist University in Bolivar, Missouri. She was the recipient of the Raymond A. Reed and Margaret H. Houk Scholarships. Cynthia began her PhD studies at Missouri University of Science and Technology in the fall of 2005. During the course of her work she received the Outstanding Graduate Teaching award. Cynthia finished her PhD in December, 2015, although she left the university and was employed as a Product Development Specialist in the R&D department at Chromaflo Technologies in Ashtabula Ohio.