NON-AQUEOUS DISPERSION POLYMERIZATION FOR AUTOMOTIVE COATING APPLICATIONS

By

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Abstract

Non-aqueous dispersion polymerization (NAD) is used to produce submicron sized particles utilized by the solvent-borne automotive coatings industry to prevent crack propagation, improve toughness and reduce energy requirements for drying. Despite its industrial significance, there have been few studies about particle nucleation and other qualities of the semibatch process. The dispersion features high solids (50-60 wt%) of higher molecular weight acrylic polymer, with the polymeric nanoparticles sterically stabilized by low molecular weight dispersant polymer chains anchored to the particle surface either by chemical or physical interaction.

The work presented in this thesis investigates three aspects influencing particle formation in the NAD system, i.e., the dispersant type, the multi-component core composition and the dispersant feeding procedure in the starved feed semibatch process. Three categories of unsaturated poly(methacrylate) dispersants are examined, a butyl methacrylate (BMA) based material with grafted vinyl functionality, vinyl-terminated BMA homopolymer macromers, and hydroxyl group functionalized macromers. The macromers provided more effective stabilization than the grafted dispersant, but the addition of 2-hydroxyethyl methacrylate (HEMA) to the dispersant reduced stability. Average particle size of the dispersion increased with the addition of methyl methacrylate and styrene to the mix of monomers used to produce the particles. The increased effectiveness of the dispersant led to an investigation of reduced dispersant levels, increased monomer loading, and simplified dispersant feeding strategies while producing small particles (<150 nm) and keeping dispersion viscosity low (<500 cp). The findings are interpreted by considering the relative polarity of the dispersant, core polymer, and solvent mixture in the NAD system.

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List of Abbreviations

AA	acrylic acid
AM	acrylamide
BMA	n-butyl methacrylate
CCT	cobalt chain transfer polymerization
$CDCl_3$	deuterated chloroform
DLS	dynamic light scattering
DMAEMA	dimethylaminoethyl methacrylate
DP	degree of polymerization
EHA	2-ethylhexyl acrylate
GMA	glycidyl methacrylate
HEA	2-hydroxyethyl acrylate
HEMA	2-hydroxyethyl methacrylate
HPC	hydroxypropyl cellulose
^1H NMR	proton nuclear magnetic resonance
MA	methyl acrylate
MAA	methacrylic acid
MMA	methyl methacrylate
MMD	molar mass distribution
MW	molecular weight
MWD	molecular weight distribution
NAD	Non-aqueous dispersion
pBMA	poly(n-butyl methacrylate)
PdI	dispersity of particle size distribution
PDMS	poly(dimethyl siloxane)

pGMA	poly(glycidyl methacrylate)
pHEA	poly(2-hydroxyethyl acrylate)
pHEMA	poly(2-hydroxyethyl methacrylate)
pMAA	poly(methacrylic acid)
pMA	poly(methyl acrylate)
p(MA/ST)	poly(methyl methacrylate-co-styrene)
pMMA	poly(methyl methacrylate)
pST	polystyrene
PSD	particle size distribution
PVP	poly(vinyl pyrrolidone)
RED	relative energy difference
SEC	size exclusive chromatography
ST	styrene
Vazo® 67	2, 2'-azobis-(2-methylbutyronitrile)
d_p	average particle size
j_{crit}	critical chain length
M_w	weight-average molecular weight
M_n	number-average molecular weight
n	refractive index
R_o	solubility radius
R_a	solubility distance
T_g	glass transition temperature
w_{inc}	weight fraction of the incorporated dispersant
wt%	weight percent
δ	solubility parameter
δ_d	dispersion force

δ_p	polar force
δ_h	hydrogen-bonding effect
η	viscosity

Chapter 1

Introduction

Non-aqueous dispersions (NADs) are structured micron and submicron sized polymer particles used for rheology control and to prevent crack propagation in solvent-borne automotive coatings. The multiphase system allows for the incorporation of high molecular weight (MW) polymer without increasing solution viscosity, and thus are a means of decreasing solvent content in the formulation.[1] The higher MW (> 30,000 Da) polymer is produced via dispersion free radical polymerization, a variant of precipitation polymerization in which the addition of stabilizer to the recipe prevents flocculation and controls the size and distribution of the polymeric particles. The method was first developed in the 1960's as a single step method for creating a micron sized dispersion of polymer particles for the top and base coat application in the automotive coatings industry in non-aqueous media.[2] Like precipitation polymerization, the system is initially homogenous but becomes heterogeneous as the reaction proceeds, since the continuous phase is a poor solvent for the polymer that is being produced. The precipitated phase consists of polymer-rich particles and the continuous phase contains miscible monomer, initiator, and soluble low molecular weight polymer (MW < 10,000 Da) used as stabilizer.

In dispersion polymerization as practiced in industry,[3] a typical NAD formulation contains polymer content of 50-60 wt%, with roughly a 1:2 ratio of stabilizer (dispersant) to core polymer. The soluble dispersant polymer is produced in a separate batch, sometimes involving multiple steps. Vinyl functionality can be introduced during dispersant synthesis, in order that the molecules become chemically attached to the NAD/microgel particles during formation. It is possible that some of the dispersant also stabilizes by physical adsorption to the particle,[4] and that some unreacted free dispersant remains in solution. The design of the dispersant and core

polymers is complex; NADs are prepared in a poor solvent (generally an aliphatic hydrocarbon medium) for the core, but a good solvent for the stabilizer. The stabilizers tend to be lyophilic acrylic copolymers, extending into the continuous phase to prevent flocculation, but are chemically attached or physically adsorbed to the lyophobic and sometimes cross-linked core copolymer.

The solids content in the industrial non-polar semi-batch NAD formulations (50-60 wt%) is at a significantly higher level than that typically (~20 wt%) used in academic batch studies of dispersion polymerization in polar solvents. Despite these differences, there are many important common features between academic and industrial dispersion systems. Particle nucleation, which controls particle number and size, is not well understood. Both heterogeneous and homogenous nucleation processes are thought to occur.[5] The polymeric surfactant is of critical importance, as it creates a reproducible polymerization system (unlike precipitation polymerization) by providing colloidal stability and helping to control average particle size and size distribution of the polymer created.[1] Solvent selection is also critical, with particle size and distribution greatly influenced by solvent composition.[6]

1.1 Thesis Objectives

Coatings are a significant cost in the automotive sector, and any advancement that can reduce costs or improve performance has an impact. Potential benefits from this study include simplified recipes and reduced cycle times for NAD production, the opportunity to reduce viscosity for the same polymer loadings and/or reduce solvent content and thus energy consumption during curing. The primary goals of the study, a systematic investigation of the role of dispersant composition and functionality, core recipe and reactor operating strategy on NAD properties, are:

1. Design and apply simplified dispersant and NAD recipes for the purpose of this academic study, and to investigate the effectiveness of grafted dispersants with varying levels of functionality compared to macromers with uniformly distributed terminal functionality.
2. Investigate the influence of dispersant feeding strategies and amounts and solvent composition on the current experimental NAD process using both grafted and macromer dispersants.
3. Explore the influence of the core compositions on the dispersion properties using both the controlled vinyl terminated macromer and grafted dispersants.
4. Compare the effectiveness of hydroxyl-containing functional macromers in dispersion polymerization to that of homopolymer macromer.

1.2 Thesis Outline

This thesis is structured as follows:

Chapter 2 summarizes pertinent literature studies of dispersion polymerizations performed in both polar and non-polar solvents, with a focus on elucidating the effectiveness of vinyl functional dispersant in the stabilization of particles, as well as survey the influence of a second monomer in dispersion copolymerization.

Chapter 3 summarizes the development of simplified grafted dispersant and non-aqueous dispersion recipes and reaction procedures, and the development of polymer and dispersion characterization methods.

Chapter 4 compares the performance of grafted and macromer dispersants for NADs synthesized with methyl acrylate homopolymer and methyl methacrylate/methyl acrylate copolymer cores.

Chapter 5 studies the influence of more complex core compositions and the dispersant amount and feeding strategy on the NAD properties, again using both the grafted and macromer dispersants.

Chapter 6 studies the effect of introducing functional BMA/HEMA macromer (compared to BMA homopolymer macromer) for the NAD preparation, and introduces the use of the Hansen solubility parameter as a means to interpret the behavior of these complex systems.

Chapter 7 summarizes the work completed, and makes recommendations for further experimental studies and theoretical frameworks to improve understanding of non-aqueous dispersion systems.

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Chapter 2

Literature Review

2.1 Dispersion Polymerization

Dispersion polymerization is an attractive method to prepare micron and sub-micron sized particles via a single step preparation for use in a variety of commercial products.[1] The probable nucleation mechanism of the system is explained by aggregation and coagulation theory, as presented in Figure 2.1:[1] (1) The polymerization starts with a homogeneous phase where monomers, initiator, dispersant (generally a polymeric steric stabilizer) and solvent are mixed well. (2) Free radicals are formed from the initiator decomposition to produce oligomers in the continuous phase. (3) The oligomers exceeding a certain critical chain length start to aggregate to produce nuclei in the continuous phase, as the medium is a poor solvent for the new polymer. (4) The coalescence continues until sufficient dispersant is attached to stabilize the particles. (5) After stabilization, the polymeric particles increase in average size by absorbing the newly initiated chains or unstable precursor particles, until the monomer is consumed. In general, the number of particles has been found to remain constant in the batch after the nucleation stage, such that the size of particles increases as a function of monomer conversion.[2]

Particle formation is observed at a low overall conversion (< 5%), with the solution changing from clear and transparent, to translucent and finally milky and opaque.[3,4] Shen et al.[5] systematically studied the nucleation mechanism of poly(methyl methacrylate) (pMMA) in an alcohol/water blend and found that the solvency of nuclei (precursor particles), i.e., the aggregation of oligomers exceeding the critical chain length (j_{crit}), was dependent on the temperature and solvent mixture. Previous work done by Cockburn et al.[4] showed that the nucleation of pMMA particles was delayed by the addition of a powerful cobalt chain transfer

agent to the system. The solvency of the oligomer and its precipitation from solution were dependent on the chain length and the medium.

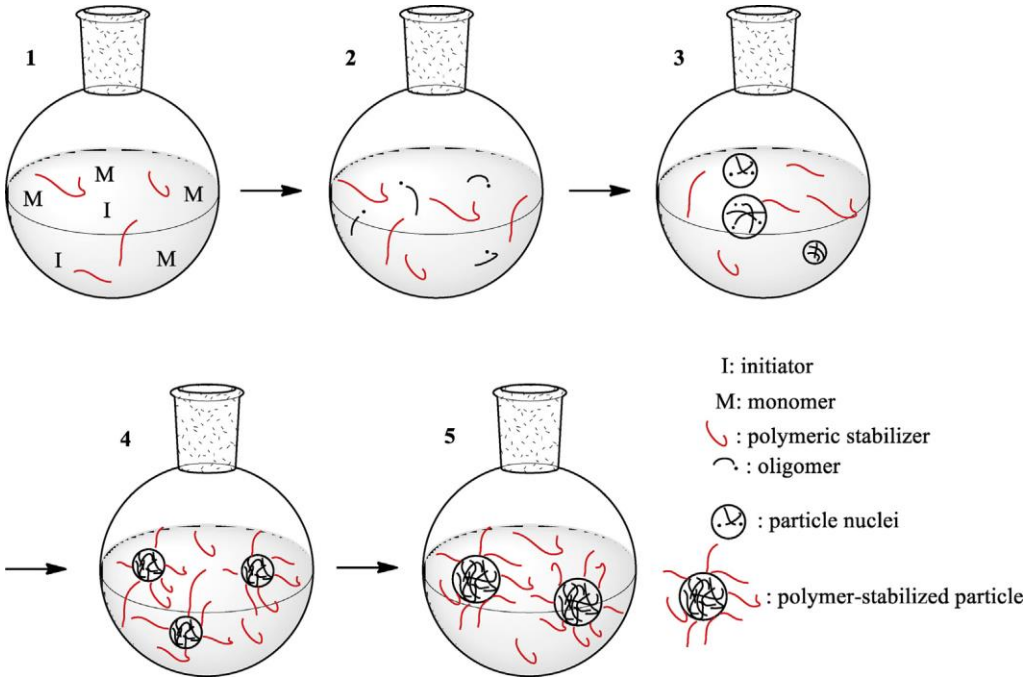

Figure 2.1 Schematic of the nucleation mechanism of dispersion polymerization.[2] **Reprinted with permission from Progress in Polymer Science. Copyright 2013, Elsevier Limited.**

Dispersion polymerization can occur within the existing particles and new chains can grow in the continuous phase, or be captured by existing particle with continued growth inside. A kinetic study of MMA radical polymerization in n-dodecane (dispersion polymerization) and benzene (solution polymerization) showed that faster polymerization rate and normally higher MW values were obtained in dispersion,[6] a result presumably due to the higher local monomer concentration and reduced termination rate (gel effect) in the swollen particle phase, as illustrated in Figure 2.2.[6] Cao et al.[3] studied the dispersion polymerization of pMMA stabilized by poly(vinyl pyrrolidone) (PVP) and found that the weight-average molecular weight (M_w) of the

polymer particles was higher than that produced in solution polymerization, while number-average molecular weight (M_n) levelled off with increased conversion, leading to a broader polymer dispersity index (M_w/M_n). This may be due to the fact that the polymerization initially happens in the solution then shifts to the particle phase after the formation of nuclei. The same molecular weight (MW) trends were also seen by Sáenz and Asua[7] in the styrene/n-butyl acrylate (BA) system. By varying the MMA/BA ratio, Jiang et al.[8] noticed that the polymerization rate of the copolymer was lower than that of BA homopolymer but closer to that of MMA homopolymer, probably due to the higher relative consumption of MMA ($r_{MMA} = 2.64$ and $r_{BA} = 0.315$), such that the initial polymerization was pMMA dominated.

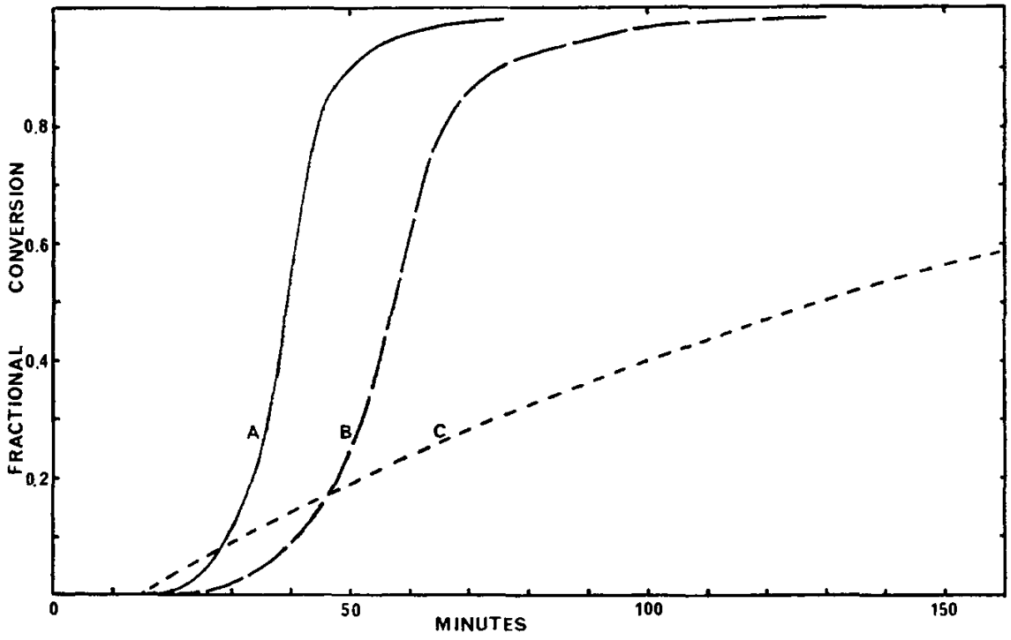

Figure 2.2 The conversion profiles of methyl methacrylate in dispersion polymerization in dodecane with stabilizer (curve A), precipitation polymerization in dodecane without stabilizer (curve B), and solution polymerization (in benzene, plot C).[6] Reprinted with permission from Journal of Polymer Science Part A. Copyright 1969, Wiley.

The dispersion polymerization of acrylates, methacrylates and styrene (ST) has been extensively studied with different types of stabilizers and solvents, usually in a batch system. As first developed for the coatings application,[9] early academic studies by Dawkins,[10] Barrett,[11] and Thomas[6] were conducted with high solids (i.e., polymer) content in alkyl hydrocarbon solvents and petroleum, with pMMA colloids stabilized by AB type block copolymer polystyrene-b-poly(dimethyl siloxane) (PDMS) copolymer, and grafted vinyl functionalized poly(12-hydroxystearic acid)-graft-glycidyl methacrylate (PHSA). An inverse correlation between the particle size and dispersant amount was seen for the pMMA particles (0.1-0.3 μm) stabilized by pST-b-PDMS.[10] Another study by Antl and co-workers[12] varied the solvent composition (hexane and high boiling point hydrocarbon) and MMA concentration with a constant monomer/stabilizer (PHSA) ratio maintained. Stable dispersions were produced with high (35-50 wt%, micron-sized particles) and low (<8.5 wt%, nano-sized colloids) monomer concentrations; however, coagulum was seen in the systems prepared with intermediate levels (8.5-34 wt%). It was said that the solvency of the polymer in its own monomer definitely played a role. Besides that, there might be a competition for the stabilizer between the nucleation and the growth of particles.

Later academic papers focus on the polymerization in mixtures of short-chain alcohols with water to obtain uniform particles (narrow dispersity in the particle size distribution (PSD)) and to investigate the influence of monomer concentration, initiator amount, stabilizer concentration and chain length, and solvent composition on polymer molecular weight, average particle size and PSD. A majority of the batch studies used common vinyl monomers, such as MMA and ST in alcohol/water solvent mixtures[13,14] or supercritical carbon dioxide ($scCO_2$).[15–17] The solids content in these studies is at a significantly lower level (~20 wt%) than that used in industrial NAD formulations (50-60 wt%). Polar organic stabilizers with labile hydrogen atoms are often used as stabilizers, such as PVP, hydroxyl propyl cellulose (HPC), poly(acrylic acid) (pAA) and poly(amic acid).[5,18–21] It has been shown that these dispersants become chemically

attached to the polymer particles through H-atom abstraction by growing oligomers to form in-situ grafts; a portion of the stabilizer may also be physically adsorbed onto the newly formed particles.[5]

Most recent research focuses on the preparation and control of mono-dispersed nano or micron sized particles for potential utilization in the electrophoretic field. Micron and sub-micron sized particles were produced with different alkyl methacrylates stabilized by PVP in methanol/water polar solvent.[22] 1 μm pMMA homopolymer particles were stabilized by PDMS type macromer in hexane[23] and the same size range of pMMA particles stabilized by a similar macromer were produced in dodecane in the presence of chain transfer agent.[24] Richez's group[24] found that the targeted particle size could be achieved not only by varying the monomer and stabilizer concentration, but also by copolymerizing with other monomers, such as vinyl pyridine and dimethylaminoethyl methacrylate (DMAEMA). Preparation procedures and characterization methods of graft PHSA type stabilizer (a troublesome dispersant to make) was documented, with the stabilizer applied to produce mono-dispersed micron-sized pMMA particles with high solids content (> 40 wt%).[25]

Besides the conventional free radical dispersion polymerization, radiation-induced and controlled radical dispersion polymerizations have also been developed. Uniform polyacrylamide (pAM) microparticles stabilized by PVP in tert-butanol/water were produced by gamma-ray radiation-induced initiation at room temperature.[26] Stable di-block poly(styrene-b-1,3-butadiene) and tri-block poly(styrene-b-1,3-butadiene-b-styrene) particles were produced by anionic dispersion polymerization in pentane, with the lyophilic moiety poly(butadiene) working as the stabilizer.[27] Reversible addition-fragmentation chain transfer (RAFT) dispersion polymerizations[28–30] have also been developed. In the aqueous phase, nano-sized poly(hydroxypropyl methacrylate) (pHPMA) particles were stabilized by soluble poly(glycerol monomethacrylate) based chain transfer agent, with larger particles formed with the increased

length of the pHPMA block.[28] Yang et al.[31] reported the preparation by atom transfer radical polymerization (ATRP) of nano-sized poly(methacrylic acid) (pMAA) particles stabilized via PVP with controlled pH values (2-4.5) of the medium.

2.2 Stabilizers Utilized in Dispersion Polymerization

The choice of dispersant is key for the dispersion synthesis, with an effective stabilizer providing sufficient coverage of the particle surface to form a steric barrier to prevent particle coagulation. The configuration of the extended lyophilic moiety in dispersant in the continuous phase is formed to overcome the thermodynamic Van der Waals force, as compared to the random-coil structure of polymer in the same solution.[32] Early attempts to develop homopolymer and random copolymer dispersants were generally not effective for low surface energy polymer particles in hydrocarbon medium, while the attempt to make grafted polyene (natural rubber) was not very successful due to the difficulty of controlling the number of vinyl groups.[11] Thus, grafted stabilizer,[25] macromer dispersant[32] and block copolymer[33] are widely applied to prepare colloids. In the non-aqueous systems, stabilizers with functional vinyl groups are favored, as covalent bonding is formed between the dispersant and the colloids in the presence of PDMS type macromer or graft PHSA type dispersants. A commercial coatings patent[34] described the development of a grafted poly(methacrylate-r-MAA-r-GMA) dispersant to stabilize nano-sized methacrylate/acrylate copolymer in heptane/mineral spirits mixture. It is this strategy that will be extensively studied in this thesis.

Takahashi and co-workers[35] systematically investigated the influence of different dispersants on micron-sized poly(2-hydroxyethyl methacrylate) (pHEMA) particles stabilized in butanol/toluene mixture applying four categories of stabilizers. pMMA homopolymer stabilizer (15 wt% relative to monomer mass) produced stable but polydisperse particles; however, mono-

dispersed particles were made with methacryloyl-terminated pMMA macromer at much lower concentration (2.5 wt%), as well as with amphiphilic vinyl functionalized graft poly(MMA-co-MAA-g-styrene) (10 wt% to monomer), and the highly unsaturated poly(styrene-b-butadiene) (10% of butadiene in the copolymer and 2.5 wt% copolymer to monomer). It was concluded that the unsaturated polymeric dispersants were more effective than those without any functionality.

2.2.1 Vinyl Functionalized and Block Dispersants

Various macromer dispersants have been applied to produce pMMA and pST particles in polar (alcohol/water) or non-polar (alkyl hydrocarbons) solvents, including poly(2-alkyl-2-oxazoline),[36] poly(ethyl glycol),[37] and PDMS.[23] Stable dispersion systems are normally produced with a low dispersant/monomer ratio, less than 20 wt%, and the quantity can go as low as only 1%. The well-controlled vinyl-terminated group among the macromer dispersant can chemically bond to the insoluble core, as the polymer chains are extended to the solvent to form the stabilizing arms. A common conclusion is drawn that mono-dispersed colloids can be produced only with a certain range of the stabilizer concentration: too low of an amount may lead to aggregation due to insufficient surface coverage provided, while too high of an amount will result in smaller and polydisperse particles when larger colloid surface can be covered. Reasons for the broader size distribution stay unclear and several possibilities are discussed as follows.

Kobayashi et al.[36] prepared mono-dispersed micron-sized pMMA particles in methanol/water solvent stabilized by end-capped styrene unit poly(2-alkyl-2-oxazoline) (PROZO), with the polarity of PROZO adjusted by the side chain, as illustrated in Figure 2.3a. Better performance (uniform particles) of the stabilizer with longer chain length and shorter side chain (methyl, ethyl to n-propyl groups) was observed, due to the better solubility of the hydrophilic moiety in the medium. Richez et al.[24] also observed the same trends, with pMMA colloids stabilized in dodecane by different MW monomethacryloxypropyl-terminated

polydimethylsiloxane macromers (5,000 and 10,000 g/mol, see Figure 2.3b). Under the same concentration (20 wt% dispersant content relative to monomer), smaller particles were produced with a longer PDMS segment, as a better barrier was provided and a larger area was occupied on the particle surface. In addition, a higher number of nuclei may be formed in the system. A different finding was seen by Klein's group[23] with the application of less concentrated (1 wt% dispersant relative to monomer) and higher MW PDMS macromer with the dual vinyl-terminated PDMS in hexane, with chemical structure shown in Figure 2.3c. The size of the pMMA particles was independent of the MW varied from 10,000 (minimum length to prepare stable dispersion) to 50,000 g/mol. It was hypothesized that in the presence of higher amounts of stabilizer, the particles nucleated over a longer period leading to a more disperse PSD. Urethane-functionalized poly(ethyl glycol)-based macromer (PEG macromer in Figure 2.3d) was used to prepare submicron sized pST particles in water/1-propanol blend through a seed-feed procedure, with a low amount of stabilizer (6-20 wt%) utilized; it was found that the grafted ratio of the macromer onto the pST was proportional to the amount of added stabilizer using proton nuclear magnetic resonance (^{1}H NMR).[37] Capek et al.[32] used methacryloyl-terminated poly(ethyl glycol) macromer to synthesize even smaller pST colloids (< 200 nm) in ethanol/water binary solvent with higher stabilizer concentrations (25 wt% relative to monomer).

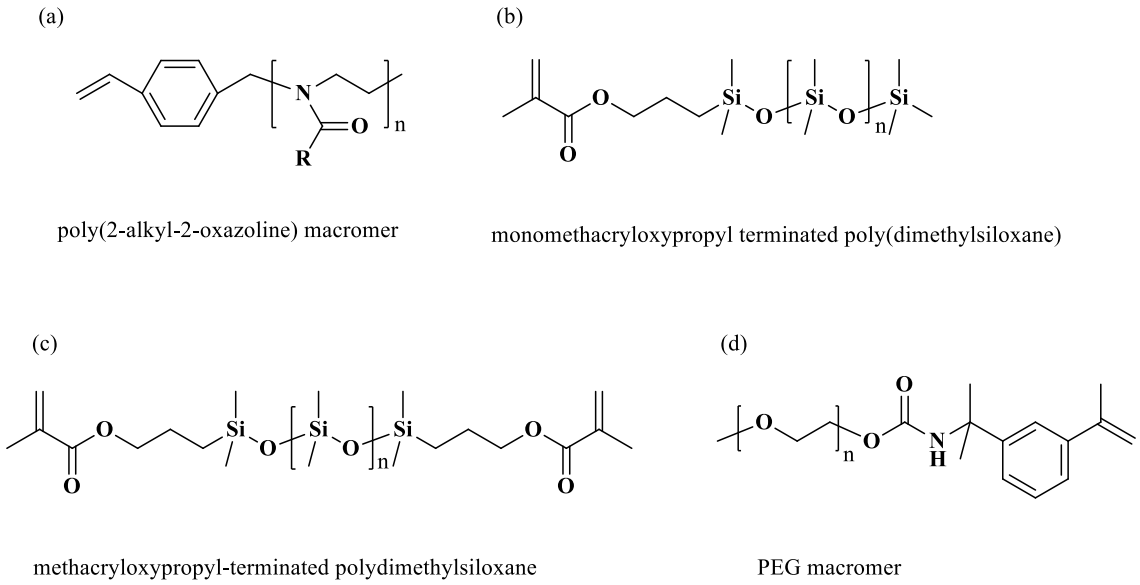

Figure 2.3 Chemical structures of some macromer dispersants utilized in dispersion polymerization studies.

The solids content in the aforementioned studies with macromer dispersants is normally under 25 wt%; with the exception of a 50 wt% mono-dispersed and micron-sized pMMA particles produced with poly(12-hydroxystearic acid)-g-pMMA (PHSA-g-pMMA).[25] This type of stabilizer can be also used to prepare micron-sized p(MMA/MAA) copolymer particles with only 5 wt% stabilizer (relative to monomer mass).[12] Cainrs and co-workers[38] showed that there were interpenetration and compression formations of the PHSA chains within a short distance range, causing the strong repulsive force between particles, as illustrated in Figure 2.4.

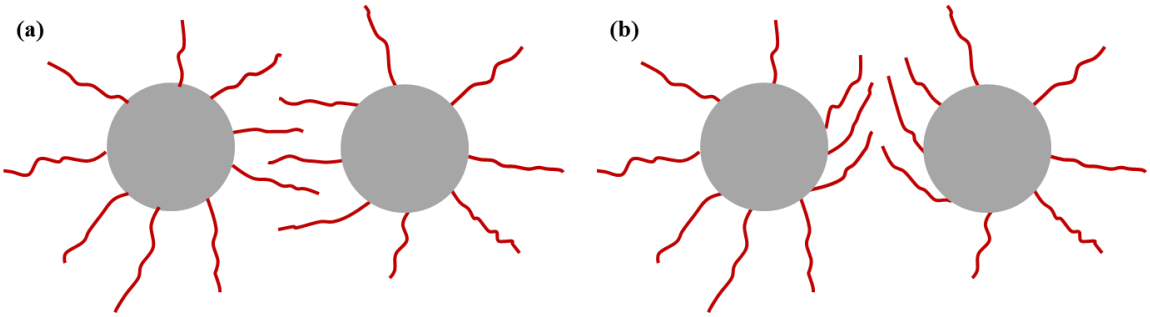

Figure 2.4 Schematic of the stabilizing polymeric chains: interpenetration and compression between the stabilizing layers.[39]

The ability of well-controlled block copolymer structures to stabilize particles has also been studied, as one component can be designed to be soluble in the continuous phase while the second component anchors to the particles to form the steric stabilization. Thus, these materials are normally non-functional and depend on physical adsorption of the stabilizer on the particle surface, but with the capability to introduce functional groups among the polymeric chains. The compatibility of the anchoring block with the core polymer should be considered, as well as the chain length and portion of the extended block in the dispersant, as these factors influence the particle size and the stability of the colloids in the dispersion. In addition, a seeded stage method is sometimes employed to the experimental procedure to prepared mono-dispersed particles: a small portion of the monomers (~10% or higher) with some solvent and initiator is polymerized for a short period (1-2 h) to form the precursor particles, with the remainder added gradually in a few hours.

Block copolymer poly(styrene)-b-poly(butadiene) was used to stabilize pST particles synthesized in pentane with controlled chain length of lyophilic polybutadiene segment; otherwise, the entanglement of the longer chains would cause the aggregation of particles.[27] Baines et al.[33] described the application of block copolymer poly(2-(dimethylamino)ethyl methacrylate-b-alkyl methacrylate) (p(DMAEMA-b-alkyl MA)) for pST in alcoholic medium,

with varied alkyl side groups (methyl, ethyl and butyl) and less concentrated anchoring portions (15 mol%) in the block compositions to provide efficient stabilization. When the stability of the colloids was tested, an interesting observation was noticed: the colloids coagulated in water but stabilized in dilute HCl, a result probably due to the protonated PDMAEMA component. pMMA particles were stabilized by tri-block isoprene-styrene-isoprene copolymer (with the lyophilic ends) in heptane, with a comparison to a differently ordered styrene-isoprene-styrene block stabilizer (with the lyophobic ends). The latter dispersant was not effective, as the soluble central isoprene block may hinder the adsorption of the terminal blocks onto the particles.[40] Narrow distributed pMMA and poly(vinyl acetate) homopolymer particles stabilized by poly(styrene-b-[ethylene-co-propylene]) in heptane were made through a seeded procedure, as a single stage preparation led to much broader PSD; an inverse relation between particle size and dispersant amount was observed.[41] Taylor and Dawkins[10] reported the production of nano-sized pMMA particles stabilized by PDMS-b-pST block copolymer in n-alkane through a seeded polymerization, as larger particles were formed in the presence of the higher portion of monomer in the seeding stage.

2.2.2 The Partition of Dispersant in a Dispersion System

It is known that dispersant associates with the core polymer, either by physical or chemical adsorption, with the excess dispersant remaining in the continuous phase. While the adsorption of the dispersant on the particle surface is preferred, there is evidence that some of the dispersant may end up in the interior of the colloids. Kawaguchi et al.[42] applied ^{1}H NMR to investigate the portion of poly(ethylene oxide) (PEO) burying inside of poly(n-butyl methacrylate) (pBMA) particles in deuterated methanol/water mixture, as a weakened intensity of the original PEO segment and a new peak were seen in the spectrum due to the immobility of the PEO in the particles. Paine's group[43] used X-ray photoelectron spectroscopy (XPS) and mass

spectrometry (MS) to quantitatively estimate the fraction of PVP on pST particles and found that the dispersant formed a patchy structure on the particle surface rather than lying flat, leaving some unoccupied space, without a significant portion of PVP inside of the particle. Similar methods were employed by Liu et al.[44] to evaluate the amount of *in situ* grafting of PEO macromer on nano-sized pST particles; it was found that 28% of the dispersant was on the particle surface among the 50% effective incorporation, another evidence of the patchy adsorption structure of the dispersant onto the particle. In addition, vinyl-terminated organic dyes can be also employed to track partition of the dispersant in the particle phase, with the measurement of intensity of the fluorescence quenching by oxygen;[45] for poly(vinyl acetate) (pVA) colloids stabilized by fluorescent group-labeled poly(2-ethylhexyl methacrylate) (pEHMA), most pEHMA was trapped within the core rather than on the particle surface.

2.3 Copolymerization in Dispersion Polymerization

The synthesis of homopolymer particles are typically investigated in dispersion polymerization studies, with less focus on more complex copolymer cores. Benefits from a second monomer may be enhanced physical properties and the introduction of functionality to the particles; however, the comonomer also can affect the size and dispersity of the particles and thus the polymerization rate and nucleation of the colloids. The relative monomer reactivity and also the corresponding polymer solubility in the solvent will influence the structure of the formed particles; and the efficacy of the stabilizer associating with the copolymer core may behave differently. Besides that, the secondary monomer can sometimes act as a co-stabilizer, with the soluble segment extending in the medium.

Most of the available literature studies examine two-component copolymer dispersions. ST was copolymerized with two acrylates (BA and 2-ethylhexyl acrylate (EHA)) stabilized by PVP in ethanol/water mixture; d_p was found to decrease with increased PVP concentration and

longer chain length, along with higher water content in the binary solvent (due to the poorer solubility of the core polymer in the medium).[46] The particle size also increased with higher acrylate content in the copolymer, but not with the choice of BA vs EHA; however the glass transition temperature (T_g) of the particle could be adjusted by the addition of the acrylate comonomers. A similar effect of the second monomer on particle size was seen when ST was copolymerized with methacrylates (GMA, MMA, and ethyl methacrylate) using a similar solvent and stabilizer.[19] Copolymerization of ST and water-soluble monomers acrylamide (AM) and acrylic acid (AA) was also studied in the same paper.[19] At low concentrations, the stabilizing function of the AM was dominating; however, at higher concentration, AM worked as an effective comonomer, increasing j_{crit} in the polar solvent and thus increasing particle size. Song et al.[47] prepared micron-sized p(ST-co-AA) particles via a two-stage method with a higher MW PVP (55,000 g/mol) as stabilizer, through delayed addition of AA to the reaction. The two-stage experimental procedure was also applied to make narrow distributed p(ST/dye-monomer) colloids, as broader size distribution was seen in the comparable one-stage batch study.[48] In addition, vinyl-terminated poly(dimethyl siloxane) macromer (PDMS) was introduced to copolymerize with ST stabilized by PVP in 2-propanol/octamethyltrisiloxane mixture to produce a hydrophobic substrate.[49] When BA was reacted with MMA in methanol/water medium, d_p increased with the increased fraction of MMA in the core and a core-shell structure (pMMA-rich core) was formed due to the high reactivity ratio of MMA (33 wt% in the copolymer).[8] As 2-(dimethylamino) ethyl methacrylate (DMAEMA) and vinyl pyridines (2-VP and 4-VP) reacted with MMA in dodecane, stable and mono-dispersed particles were produced with PDMS type macromer.[24]

The addition of a small amount of cross-linker, both ethylene glycol dimethacrylate[46] and divinyl benzene,[13] has been found to produce monodisperse particles with smooth surface.

However, the weight fraction of cross-linker should be controlled; otherwise, severe irregularity or coagulation may happen because of different cross-linking densities in the microspheres.[46,50]

2.4 Conclusions

Numerous studies have focused on the dispersion polymerization in alcohol/water mixtures to make micron-sized particles, with the stabilizing dispersant either physically adsorbing to the particles or reacting via a H-atom abstraction mechanism. There is emerging attention on the preparation of mono-dispersed particles in the hydrocarbon medium, with vinyl functionalized dispersants. However, most studies are carried out at low solids content in batch reactors, regardless of the dispersant used. Only a few efforts have attempted to quantify the incorporated dispersant on particles, as the associated experimental procedures are difficult.

Extensions to copolymer systems demonstrate that the reactivity and the solvency of each monomer influence the final dispersion particle size and distribution, as well as polymerization rate and physical properties (T_g, for example). However, there is little available information regarding the production of more complex multi-component core formulations under high solids conditions, the focus of this study.

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Chapter 3

Preliminary Study of Reaction Conditions of Grafted Dispersant on NAD Properties

3.1 Introduction

Structured particles are a key part of solvent-borne coatings technology platform, and are expected to grow in importance as a means to increase polymer loadings without increasing viscosity. These particles reduce crack propagation, and enhance toughness, spray efficiency and physical drying in the application.[1] The particles can be designed to contain a variety of functional groups that could expand their use in a wider range of materials. In addition, controlling the type of functionality and the distribution of said functional groups can lead to a better understanding of the relationship between polymer architecture and finished product performance.

Starting from a patent description, simplified recipes for both dispersant and non-aqueous dispersion (NAD) are developed in this chapter, as well as the experimental procedures to produce and characterize NADs. Dispersants with different levels of functional vinyl groups were employed, as the performance of corresponding NADs was evaluated. Besides that, the effects of reaction conditions, such as dispersant amount, feeding strategy, monomer concentration and solvent composition, were explored.

3.2 Experimental

All experiments were carried out in a l liter semi-batch reactor which has been intensively used in our group.[2,3] A two-step procedure was executed to produce the stable polymer particles, starting with the production of the dispersant polymer.

3.2.1 Materials

The monomers, n-butyl methacrylate (BMA, Sigma-Aldrich, 99%), methacrylic acid (MAA, Sigma-Aldrich, 99%), glycidyl methacrylate (GMA, Sigma-Aldrich, 97%), methyl methacrylate (MMA, Sigma-Aldrich, 99%), methyl acrylate (MA, Sigma-Aldrich, 99%), isobornyl methacrylate (IBMA, Sigma-Aldrich, technical grade), styrene (ST, Sigma-Aldrich, ≥99%), n-butyl acrylate (BA, Sigma-Aldrich, ≥99%) and 2-hydroxyethyl acrylate (HEA, Sigma-Aldrich, 96%), were used as received. The initiators, t-butyl peracetate (TBPA, Sigma-Aldrich, 50 wt% in mineral spirits) and 2, 2'-azobis-(2-methylbutyronitrile) (Vazo® 67, E. I. du Pont), were also used without any purification. The inhibitor and the amino catalyst, catechol (Sigma-Aldrich, ≥99%) and 2-dimethylamino-2-methyl propanol (Sigma-Aldrich, 80 wt% in water), were utilized as they are, respectively. The solvents, isopropanol (Sigma-Aldrich, 99.5%), xylenes (Sigma-Aldrich, ≥98.5%), m-xylene (Sigma-Aldrich, ≥99%), heptane (Sigma-Aldrich, ≥99%), butyl acetate (Sigma-Aldrich, ≥99%), mineral spirits (Sigma-Aldrich) and tetrahydrofuran (THF, Sigma-Aldrich, ≥99.9%), were used without any purification.

3.2.2 Solution Polymerization of Dispersant Polymer: Commercial Recipe and the Standard Simplified Recipe

The recipe of commercial dispersant is complex (6 monomers for copolymerization), as presented in Dupont's patent.[4] The dosing amount had been scaled down to fit our reactor, as stated in the followed paragraph. 178.7 g of xylenes was added to the reactor and the temperature

was raised to 138 °C. A pre-mixed solution of 95.5 g ST, 98.5 g BMA, 96.8 g BA, 52.8 g HEA, 9.8 g MAA, 65.4 g IBMA, 25.4 g TBPA and 67.3 g xylenes was pumped to the reactor at a constant rate over 240 min, after which the mixture was kept at 138 °C for another 30 min. A mixture of 0.016 g catechol and 0.18 g isopropanol, 7.4 g GMA and 0.1 g 2-dimethylamino-2-methyl propanol were added in order. The reaction was hold at 138 °C for 120 min and then cooled to room temperature.

Only two monomers (BMA and MAA) are utilized in the simplified recipe developed in this work. The expected solids content, number of functional vinyl groups and molecular weight (MW) of dispersant are kept the same as in the patent. The amount of initiator was lowered by 60% to maintain the target weight-average MW of 6000-8000 Da. 178.7 g xylenes was added to the reactor and heated up to 138 °C. A mixed solution of 409.7 g BMA, 9.8 g MAA, 15.0 g TBPA solution and 67.3 g xylenes was pumped to the reactor over 240 min and kept at 138 °C for another 30 min. A mixture of 0.016 g catechol and 0.18 g isopropanol, 7.4 g GMA and 0.1 g 2-dimethylamino-2-methyl propanol were added in order and hold at 138 °C for 120 min and the reactor was cooled to room temperature.

3.2.3 Dispersion Polymerization of the Commercial NAD and the Standard Simplified NAD

There were six monomers used in the commercial NAD recipe described in the patent.[4] 128.2 g dispersant polymer solution (63.6 wt% solids content), 15.3 g isopropanol, 35.3 g mineral spirits and 79.5 g heptane was added to the reactor and heated to 92 °C. A mixed solution of 32.3 g ST, 43 g HEA, 80 g MMA, 3.3 g GMA, 8.6 g MAA, 37.7 g MA, 19.2 g heptane, 19.7 g mineral spirits, 64.4 g dispersant polymer and 1.8 g Vazo® 67 was fed to reactor at constant rate over a period of 210 minutes and held at 92 °C for an additional 45 minutes. A solution of 0.6 g Vazo® 67 and 9.8 g butyl acetate was added over 30 minutes and then held at 92 °C for 60 minutes.[4]

Two monomers are introduced to prepare the standard simplified recipe. The molar ratio between MMA and MA, the solids content and weight fraction of dispersant are kept the same as prepared in the patent. 128.2 g simplified dispersant polymer solution and 130.1 g heptane were added to the reactor and heated to 92 °C. A pre-mixed solution of 4.3 g butyl acetate and 0.32 g Vazo® 67 was added as a shot before polymerization started. A solution of 139.2 g MMA, 65.8 g MA, 48.7 g heptane, 64.4 g dispersant polymer solution and 2.5 g Vazo® 67 was fed to reactor during 210 minutes, with the dispersion held at 92 °C for a further 45 minutes. A solution of 0.82 g Vazo® 67 and 9.8 g butyl acetate was added over 30 minutes and then held at 92 °C for 60 minutes. The dispersion was cooled down to room temperature.

3.3 Characterization

3.3.1 Conversion/^{1}H NMR /SEC

Conversion is determined by gravimetry. Approximately 1 mL samples were taken at specified times during the reaction and cooled immediately in the refrigerator. They were air dried for 4 hours at room temperature and then in the vacuum oven at 60 °C for 24 h. Conversion was calculated by the ratio between the polymer mass after drying to the initial weight of the sample multiplied by the known weight fraction of monomers.

Proton nuclear magnetic resonance (^{1}H NMR) was used to qualitatively verify the presence of reactive double bonds on the functionalized dispersant. Spectra were measured using a Bruker Acance-400 MHz spectrometer with automation on dried polymer dissolved in deuterated chloroform ($CDCl_3$).

Polymer MW averages and molecular weight distribution (MWD) were analyzed by size exclusive chromatography (SEC) using a Waters 2960 separation module followed by a Waters

410 differential refractometer (DRI). THF was used as eluent at a flow rate of 1.0 mL·min^{-1} through four Styragel® columns (HR 0.5, 1, 3, 4) operated at 35 °C. DRI detector was calibrated by 10 narrow MWD polystyrene standards with MW from 870 to 355,000 Da.

The Mark-Houwink (MH) parameters applied to calculate dispersant and dispersion MWs from the RI output using the principal of universal calibration are provided in Table 3.1. The dispersant MW values are not corrected for the presence of MAA, as the comonomer content is low (5 mol%) and no MH parameters are available because of the insolubility of poly(methacrylic acid) (pMAA) in THF; thus, dispersant MWs are calculated using MH values of pBMA. Dispersion MWs are calculated assuming copolymer (MA/MMA) composition is equal to the feed composition, a reasonable assumption for starved-feed operation.

Table 3.1 Mark-Houwink parameters for MW calculation in THF at 35 °C.

Polymers	K($\times \mathbf{10^{-4}}$) (dL·g^{-1})	a	Ref.
pST	1.14	0.716	[5]
pBMA	1.48	0.664	[5]
pMMA	0.944	0.719	[6]
pMA	1.95	0.660	[7]

3.3.2 Particle Size and Size Distribution

Average particle size and size distribution were measured on Malvern Zeta-Sizer Nano ZS using dynamic light scattering (DLS) with an angle of 173°. The method developed has been modified from standard operating procedures (SOP) provided by Axalta Coating Systems; these modifications were needed as the dispersion particles produced in this work are not cross-linked and thus are soluble in xylenes. All the analyses were carried out at 25 °C in a quartz cuvette with

a dilution of a solvent heptane/xylene mixture (1:1, w/w). The Grunberg and Nissan equation (Equation 3.1)[8] and the Lorentz-Lorenz formula (Equation 3.2)[9] are applied to estimate refractive index (n_m = 1.418) and viscosity (η_m = 0.562 cP) of the binary solvent mixture. Table 3.2 shows the values for pure components at 25 °C. The refractive index of polymer dispersion is 1.59, as provided by Axalta.

$$\frac{n_{12}^2-1}{n_{12}^2+2} = \phi_1 \frac{n_1^2-1}{n_1^2+2} + \phi_2 \frac{n_2^2-1}{n_2^2+2} \tag{3.1}$$

$$\ln \eta_m = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G_{12} \tag{3.2}$$

In Equation 3.1, n_m, n_1 and n_2 are the refractive indices of the solvent mixture, pure solvent 1 and pure solvent 2; ϕ_1 and ϕ_2 are volume fractions of solvent 1 and solvent 2 calculated from known densities assuming volumetric additivity. In Equation 3.2, η_m, η_1 and η_2 are the viscosities of solvent mixture, pure solvent 1 and pure solvent 2, respectively; x_1 and x_2 are the molar fractions of the solvents respectively; G_{12} refers to the interaction parameters which is a function of the components 1 and 2 as well as temperature, estimated by the group contribution method proposed by Isdale et al.[10]

Table 3.2 Viscosities and refractive indices of pure component at 25 °C.

Liquid	η (cP)[a)]	n[a)]
o-xylene	0.76	1.51
m-xylene	0.59	1.50
p-xylene	0.61	1.50
heptane	0.39	1.39

a) These sets of data are available in Nanotrac U1714E Microtrac Inc at Axalta Coating Systems.

Table 3.3 Average particle size and size distribution of standard dispersion (NAD II) measured in different heptane/xylenes solvent compositions.

Sample	wt. fract. of heptane	d_p (nm)	PdI
NAD II-10 wt%	0.1	193	0.17
NAD II-20 wt%	0.2	154	0.15
NAD II-30 wt%	0.3	146	0.14
NAD II-40 wt%	0.4	140	0.14
NAD II-50 wt%	0.5	134	0.14
NAD II-60 wt%	0.6	135	0.16

It was found that the polymer produced using the simplified dispersion recipe dissolved in xylenes and that the particles settled out of heptane, such that a mixed solvent is needed. The effect of solvent composition was investigated using NAD II, a dispersion prepared according to our standard simplified recipe. Unimodal particle size distributions (PSDs) were found for 0.1-0.6 weight fraction of heptane in the solvent mixture, as presented in Figure 3.1. Average particle size (d_p) and dispersity of particles (PdI) are summarized in Table 3.3, with d_p plotted in Figure 3.2. Particle size is relatively constant between 20 and 60 wt% heptane, and a mixture with 50 wt% heptane was chosen for all further particle size analyses. Bimodality in the PSD arises from solvent mixture with weight fraction of heptane ≥ 0.7, as shown in Figure 3.3.

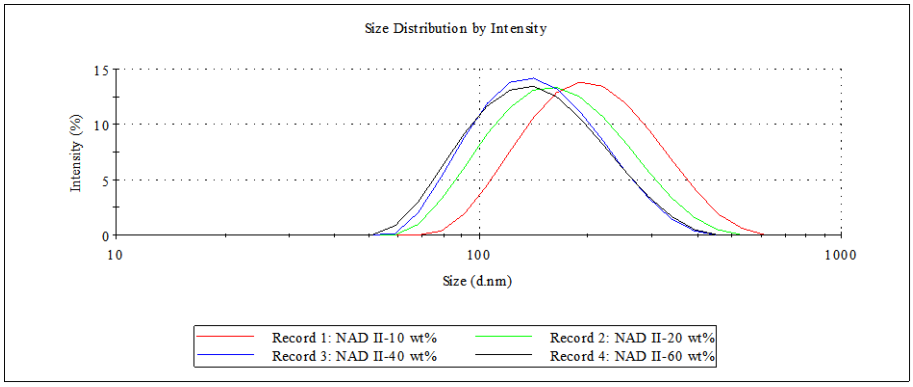

Figure 3.1 Particle size distribution of the standard simplified NAD in 10-60 wt% of heptane in the binary solvent.

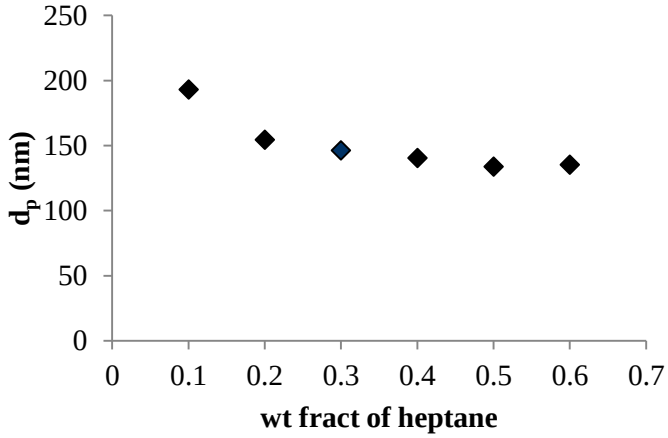

Figure 3.2 Average particle size of the standard NAD in different weight fractions of heptane.

Repeatability of the SOP was tested on the standard NAD and a commercial NAD (RC7121, supplied by Axalta) on two different days. The repeat values were identical (within 1 nm) at 133 and 233 nm for the two samples, as each reported value is actually an average of three measurements. The comparisons are plotted in Figure 3.4 and Figure 3.5; despite the identical averages, there is a noticeable difference in the shapes of the repeat measurements for RC7121; as these particles settled in the binary solvent, the sample was characterized in m-xylene. These

results demonstrate the consistency of the measurement method, which is applied throughout this study to determine average particle size and PSD, the latter quantity usually reported in terms of dispersity.

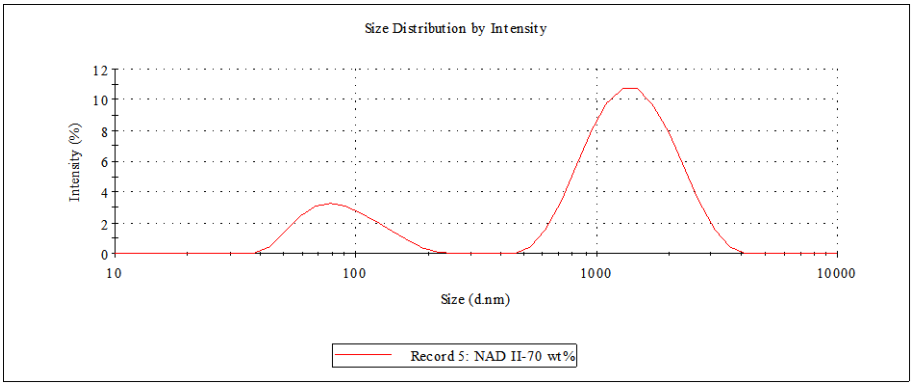

Figure 3.3 Particle size distribution of the standard NAD in 70 wt% heptane in heptane/xylenes mixture.

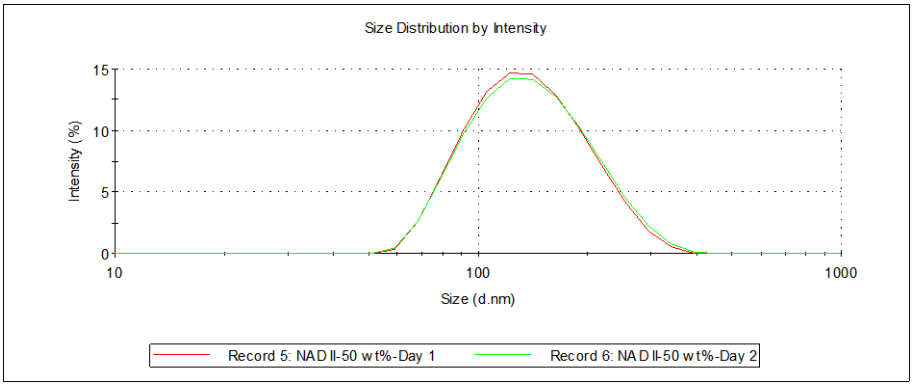

Figure 3.4 Repeatability of particle size distributions of the standard NAD in 50 wt% heptane.

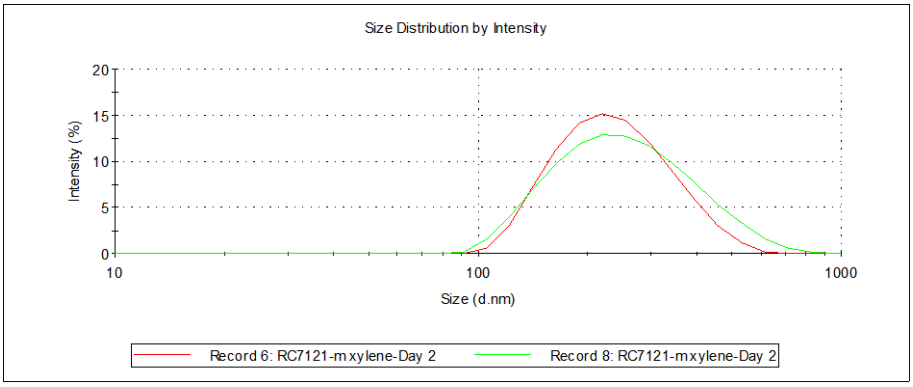

Figure 3.5 Repeatability of particle size distributions of the commercial NAD in m-xylene.

3.4 Results and Discussion

3.4.1 Free Radical Polymerization of BMA/MAA/GMA to Produce Dispersant

Controlling the number of functional vinyl group per dispersant polymer chain is important to have a soluble and effective stabilizer.[1] On average there is one carboxyl group per chain for the dispersant described in the Dupont patent (average chain length of 20 monomer units, with 5 mol% MAA).[4] Free radical starved-feed copolymerization of BMA and MAA is first completed to create chains of average length of 20, followed by the esterification between the carboxyl group (of MAA) and epoxy group (of GMA) to produce a functional unsaturated dispersant. The scheme of esterification is given in Figure 3.6.[11]

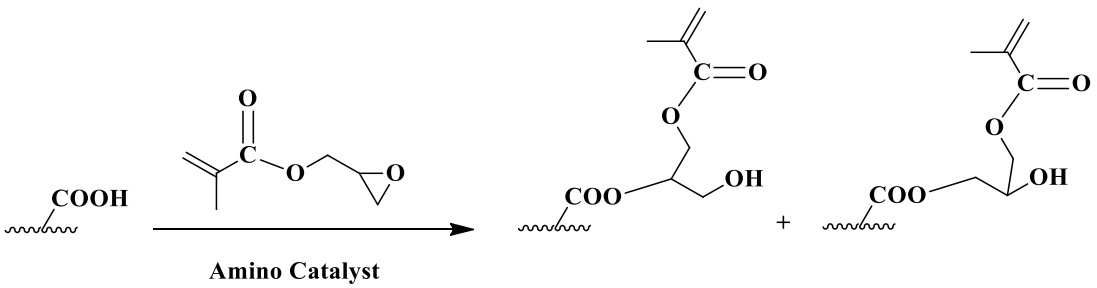

Figure 3.6 Schematic of the reaction between carboxyl and epoxy groups to form reactive grafted dispersant.

Table 3.4 Dispersants produced with different molar ratio between GMA and MAA.

Sample	GMA/MAA molar ratio	M_n (Da)	M_w (Da)
Dispersant I	0	3200	6400
Dispersant II	0.5	4000	8100
Dispersant III	1.0	3900	9200

As presented above, the simplified recipe developed is a solution polymerization of BMA and MAA (5 mol%) produced at the operating conditions (2.1 $g \cdot min^{-1}$ monomer feed, as scaled to our 1 L reactor) specified by the patent. Three versions of dispersant were made, with the average number of vinyl groups per chain varied by the different molar ratio between GMA and MAA, as described in Table 3.4. The expected average number of double bonds per chain is 0, 0.5 and 1, respectively, based on polymer MWs and assuming quantitative reaction of GMA with MAA according to Figure 3.6. M_w increases with reaction time over the semi-batch feeding period, as plotted in Figure 3.7. The good agreement between the three experiments illustrates the reproducibility of the reaction, as the base recipe (before GMA addition at 270 min) is the same for all three dispersants. The dispersant polymer M_w increases slightly (from ~7000 to 8000-9000 Da) upon addition of GMA, with the dispersant synthesized with the highest GMA amount (1:1 ratio with MAA) reaching the highest M_w. The increase may be caused by the reactions involving unconverted BMA, which does not reach 100% conversion (Figure 3.8) due to a ceiling temperature effect.[12] This extra monomer may lead to some crosslinking between chains, as suggested by the increased fraction of higher MW chains seen for Dispersant III compared to Dispersant I in the MWDs plotted in Figure 3.9.

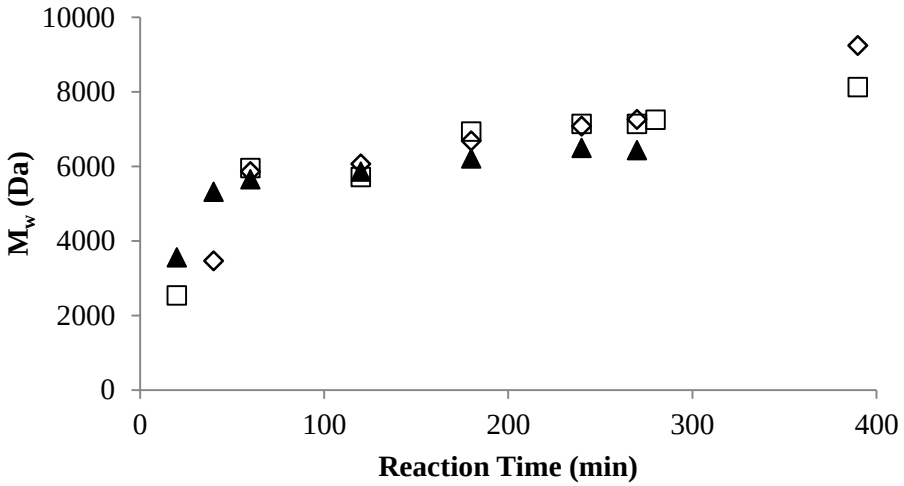

Figure 3.7 Weight-average molecular weight of dispersants made with different molar ratio between GMA and MAA: Dispersant I (closed triangle symbols), Dispersant II (open square symbols), and Dispersant III (open diamond symbols).

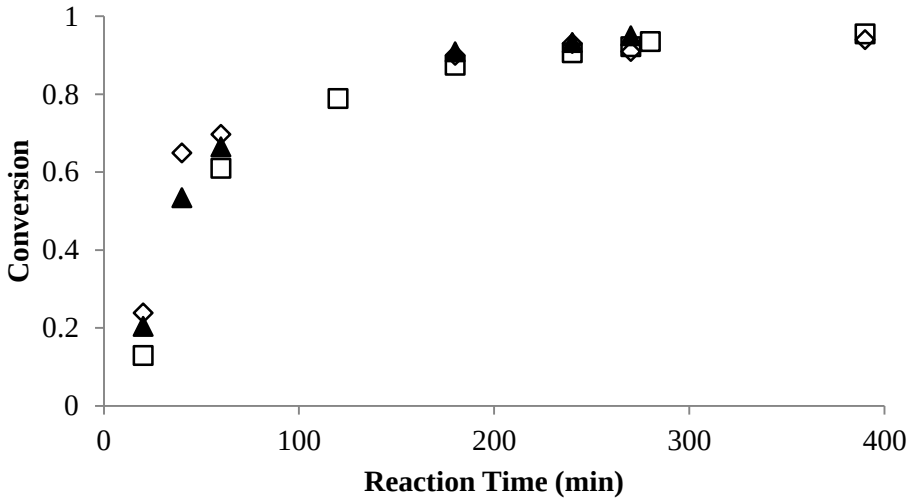

Figure 3.8 Monomer conversion during semibatch production of dispersants: Dispersant I (closed triangle symbols), Dispersant II (open square symbols), and Dispersant III (open diamond symbols).

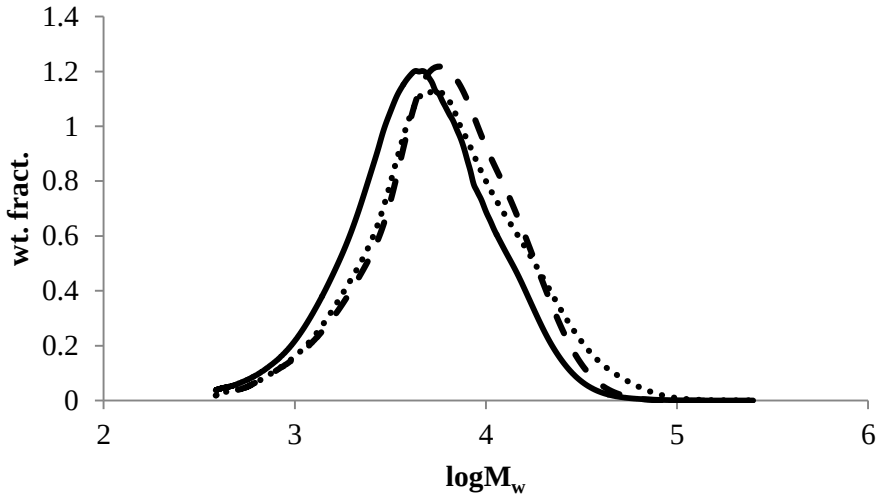

Figure 3.9 MWDs of the final dispersant products: Dispersant I (solid line), Dispersant II (dashed line), and Dispersant III (dotted line).

The addition of the double bond to the dispersant by the epoxy-carboxyl reaction is verified by ^{1}H NMR, as presented in Figure 3.10. The singlet at 5.5 ppm is the only difference between before and after the addition of GMA, and thus may be an indication of the incorporation of double bonds to the chain (see inset figure). However, the technique cannot quantitatively determine the fraction of vinyl groups of dispersant because of the weak signal.

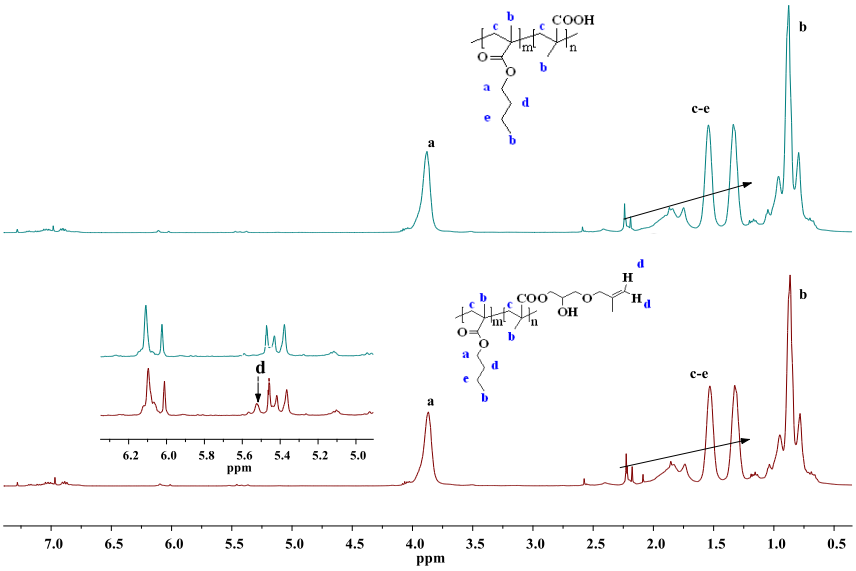

Figure 3.10 ^{1}H NMR Spectra of Dispersant II before (top) and after (bottom) the addition of GMA. The inset is a blow-up of the double-bond region.

3.4.2 Dispersion Polymerization of MMA/MA as the Core Polymer

The dispersants were used in the synthesis of the dispersion products, following the experimental procedures outlined earlier in the chapter. A portion of the dispersant is added to the reactor at the start of the reaction, with the remainder (mixed with the monomer feed) fed to the reactor. The initiator shot added to the reactor before the monomer feed is required to build up initiator concentration at the beginning of the batch and to react with any inhibitor that is added with the dispersant. Otherwise an unstable NAD system is resulted, with particles settling out from the continuous phase, as depicted in Figure 3.11. The initiator shot is also used in semibatch emulsion polymerization to nucleate particles quickly and produce stable latex.[13]

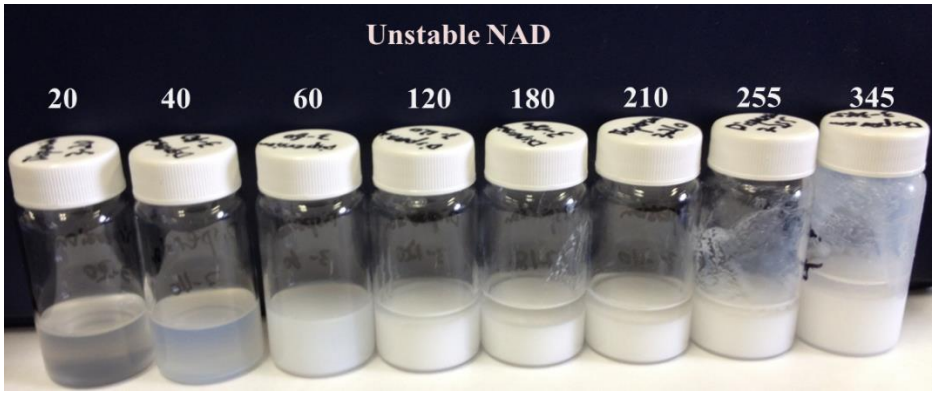

Figure 3.11 Image of unstable NAD produced without the initiator shot.

Three versions of NAD were made using the same dispersion recipe, with the only change being the dispersant used, as listed in Table 3.5. Images of NAD samples taken during the polymerization period are shown in Figure 3.12. The liquids are all clear at 20 min, then translucent at 40 min, and milky and opaque after 60 min. Nucleation of polymeric particles occurs at the early stage of polymerization as observed by other researchers on dispersion polymerization in polar medium.[14] The final conversion of the three NAD final products is close to 100% with high solids content (59 wt%) and low viscosity (easily pourable).

The MW averages of the NAD products are summarized in Table 3.5; the value for NAD III could not be determined, as the polymer dissolved in THF could not pass through the nylon filter during sample preparation. It is likely that the polymer is partially cross-linked, due to the reaction of dispersant (some chains containing more than one double bond) with the growing MMA/MA copolymer chains. M_w of NAD II made with Dispersant II (with a higher vinyl group content) is higher than NAD I made with Dispersant I (unfunctionalized). This result may be partially attributed to the differences in dispersant MWs, as also reported by Kongsupapsiri's group[15] for the copolymerization of ST and acrylates utilizing different MW PVP samples as the stabilizer. However, the increase in MW values also is most likely due to the functional vinyl

groups of Dispersant II reacting with MMA/MA copolymer chains to form chemical anchors on the particle surface. This reaction will not occur with Dispersant I, as no double bonds were introduced to the dispersant chains.

Table 3.5 MWs of three versions of NAD made with different dispersant.

Sample	Made with Dispersant	M_n (Da)	M_w (Da)
NAD I	I	8500	44000
NAD II	II	10100	64100
NAD III	III	-	-

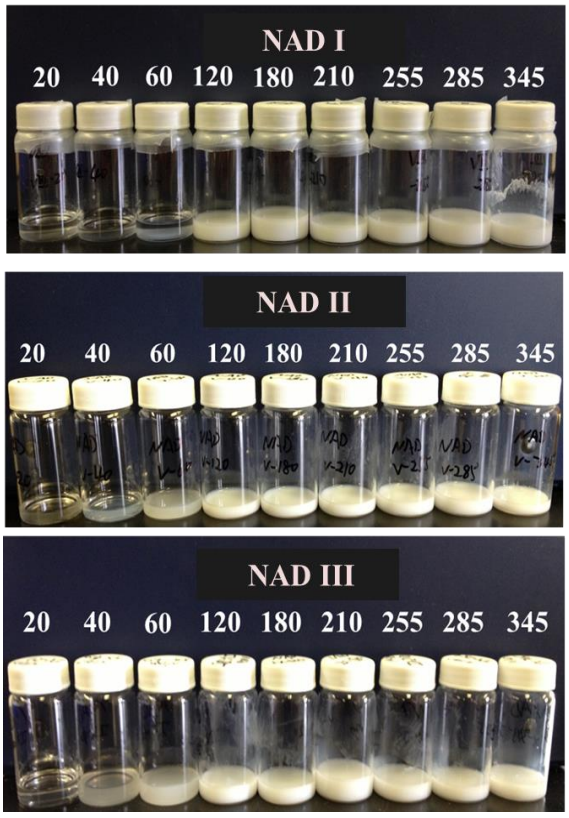

Figure 3.12 Images of NAD samples taken during the polymerization period.

One of our objectives is to make stable NAD with a reduced amount of free dispersant in solution such that the viscosity of the NAD system will be lowered, making it easier for rheology control. It is certain that there is free dispersant (chains that are neither chemically anchored or physically adsorbed to the particle surface) in the continuous phase, as demonstrated by El-Aasser et al.[16] An indirect method to quantify the free surfactant was explored, based on the overlapped area between the plots of NAD and dispersant polymer MWDs. As shown in Figure 3.13, the lower MW peaks from the NADs occur at the same position as the dispersant MWDs, indicating the presence of free dispersant that is not incorporated in polymer particles. Thus we tried to quantify free dispersant by calculating the relative areas of the two peaks (attributed to free dispersant vs dispersion) from the SEC traces.

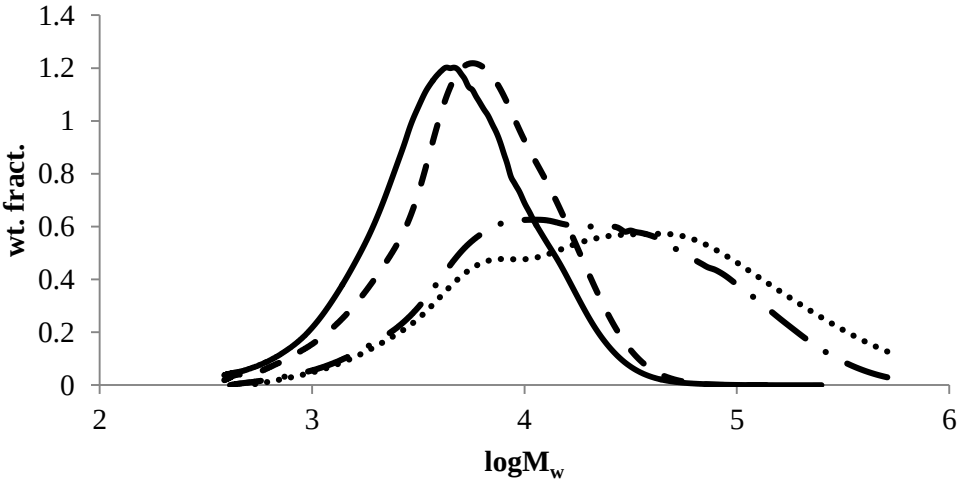

Figure 3.13 MWDs of dispersants and NADs: Dispersant I (solid line), Dispersant II (dashed line), NAD I (dash-dot line) and NAD II (dotted line).

The NADs produced exhibit a broad polydispersity and bimodal MWDs, as shown in Figure 3.13. It is reasonable to assume that the lower MW shoulder zone belongs to the free

dispersant. It is facile to normalize the height of this peak with that of the dispersant MWD, as presented in Figure 3.14. After normalization, a clear difference can be seen between the MWDs of NAD I (produced with dispersant without vinyl groups) and NAD II (standard dispersant with reactive groups): the relative height and area of the higher MW peak for NAD II increases more than that for NAD I, providing a qualitative indication that the dispersant is being incorporated (through chemical reaction) into the NAD particles. While the position of the low MW (dispersant) peak remains constant for NAD II, it shifts slightly to higher value for NAD I. Although the SEC method provides qualitative evidence of a significant fraction of unreacted dispersant, with the fraction reduced in the presence of the reactive double bonds, the amount could not be quantified from the SEC traces. Thus, this set of experiments was repeated in Chapter 4, after which a more quantitative measurement of unreacted dispersant was developed.

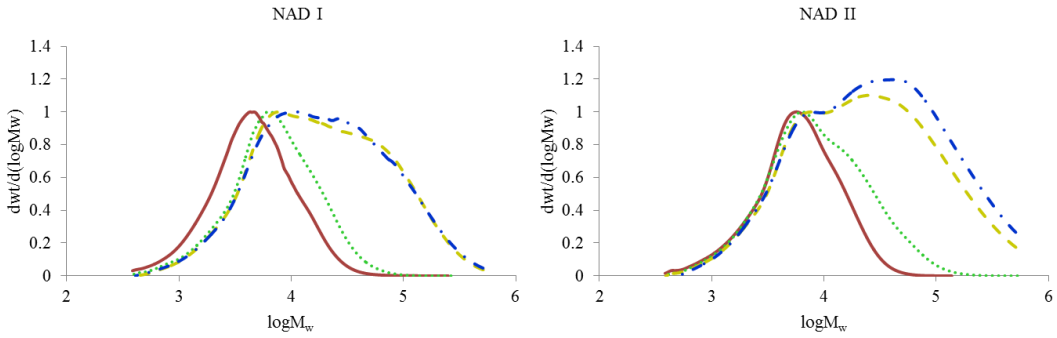

Figure 3.14 Normalized MWDs of Dispersants and NADs, left: Dispersant I (solid line), NAD I-60 (dotted line), NAD I-180 (dashed line) and NAD I-345 (dash-dot line); right: Dispersant II (solid line), NAD II-60 (dotted line), NAD II-180 (dashed line) and NAD II-345 (dash-dot line), with the 'xxx' suffix in NAD I-xxx and NAD II-xxx indicating the semi-batch reaction time at which the sample was collected.

Table 3.6 Average particle size and size distributions of NADs made with different dispersants.

Sample	d_p (nm)	PdI
NAD I	197	0.22
NAD II	134	0.17
NAD III	152	0.23

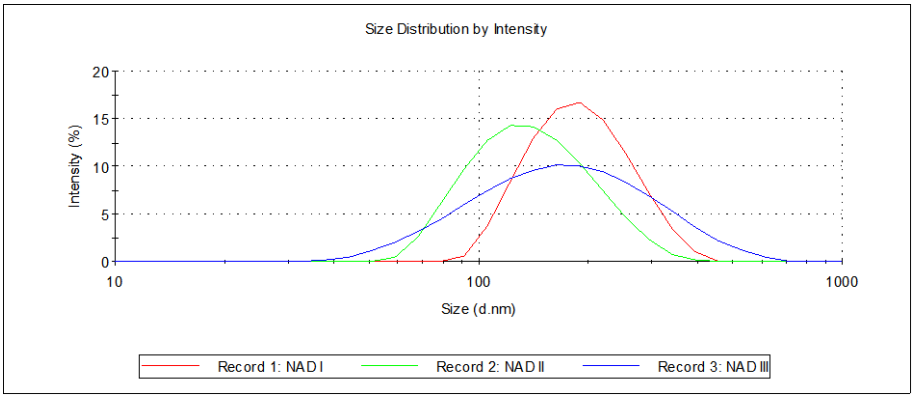

Figure 3.15 PSDs of NADs made with different dispersants: NAD I (red line), NAD II (green curve) and NAD III (blue curve).

Table 3.6 summarizes the particle size of the final NAD samples, with unimodal PSDs observed for all three products, as shown in Figure 3.15. Smaller particles are formed with reactive dispersant (NAD II and III) compared to NAD I, as the dispersant is chemically attached to the surface of the particles. It is surprising, however, that slightly smaller particles were formed with NAD II compared to NAD III, which has a higher concentration of functional groups (reactive double bonds) in the dispersant. Since the weight fraction of dispersant and other factors (monomers, initiator and solvent) in dispersion preparation is the same, it may be caused by the higher functionality of the dispersant, leading to multiple attachments on the particles (consistent

with the inability to filter NAD III dissolved in THF for SEC analysis), which reduces its effectiveness.

The other element of interest is whether the average particle size produced by the simplified recipe developed in this thesis is the same as that of DuPont commercial product (multi-monomer recipe with cross-linked particle core, RC7121). Our cross-linked NAD is a sample made in the laboratory using the simplified MMA/MA recipe with the addition of a small amount of GMA (1.6 wt%) and MAA (4.2 wt%) in the core. Average particle size of the two NADs is in the same range, as d_p of our cross-linked NAD (251 nm) is slightly larger than that of the commercial NAD (225 nm).

3.5 The Effect of Reaction Conditions on NAD Properties

As studied in batch dispersion systems in the literature, monomer, initiator, dispersant and solvent all affect the particle size and size distribution.[17,18] Here we present some investigations of the experimental semibatch procedure, varying the amount of dispersant and feeding method, as well as the monomer amount (solids loadings) and solvent composition (heptane/xylenes ratio). Dispersant II, with half of MAA functionalized with GMA, was employed in these sets of experiments.

The solids content (non-volatile dry ingredients) of the base NAD recipe is 60 wt%, consisting of 40 wt% core (monomer added during the NAD recipe) and 20 wt% dispersant. NADs were prepared with reduced amounts of dispersant solution, starting with a reduction of 25 wt%, to 35 wt% and up to 50 wt% of the base amount while the feeding strategy of the dispersant remained unchanged.

Table 3.7 MWs and average particle size of NADs prepared with different amount of dispersants.

wt% of dispersant	M_n (Da)	M_w (Da)	d_p (nm)	PdI
Standard	6700	60500	134	0.18
25% less dispersant	7000	69600	144	0.15
35% less dispersant	11300	107300	154	0.20
50% less dispersant	14200	138700	157	0.20

With the reduced amount of dispersant, NADs with larger particles and higher M_w are produced compared to the standard NAD (69500 Da and 134 nm). As summarized in Table 3.7, M_w increased by a factor of two as the dispersant amount is reduced to 50 wt% less, with the particle size increasing by 20 nm. Batch dispersion studies have shown that faster conversion rates and molecular weights are seen in dispersion polymerization, as compared to solution polymerization due to the change in the principle location of reaction (from solution to the continuous and the particle phases).[19,20] Earlier nucleation of fewer particles is likely occurring when less dispersant is utilized in the formula, leading to the higher M_w and the larger particles.[17]

The standard feeding method is 2/3 of the dispersant added before polymerization, with 1/3 fed with monomer loading. Two simpler approaches of the addition of dispersant have been explored as part of the preliminary investigations reported in this chapter; the first is by adding all the dispersant initially at the start of polymerization and the second is by feeding all the dispersant with the monomer loading (no initial charge). Figure 3.16 demonstrates that the lowest M_w and smallest particles are produced with the standard feeding strategy, with the highest M_w and largest particles obtained for NAD made with all dispersant fed with monomer, and a slight increase of M_w and d_p noticed for NAD prepared with all of the dispersant added initially. It is

reasonable to hypothesize that earlier nucleation occurs without the presence of dispersant at the start of the reaction, and with a lesser amount of dispersant present to sterically stabilize the particles, larger particles are formed. Following this argument, with all the dispersant added at the start of polymerization, a delayed nucleation should be observed resulting in smaller particles. However, as shown in Figure 3.16, such is not found here, as particle size is roughly the same as that of the standard feeding strategy. Further investigations on feeding strategy are reported in Chapter 5.

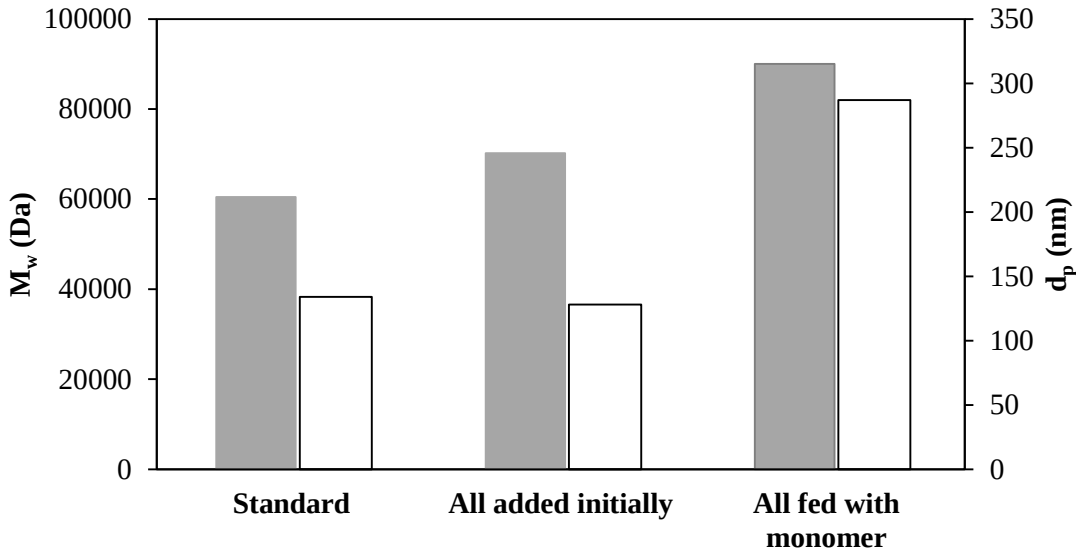

Figure 3.16 Weight-average molecular weight and average particle size of NADs made with three different feeding strategies: M_w (filled bars) and average particle size (unfilled bars).

As a third variation to the base case recipe, the total amount of monomers (MMA/MA) fed to the dispersion is increased by 25 wt% and 35 wt% (total solids content in recipes of 63.6 wt% and 64.9 wt%, respectively); all other aspects of the recipe (including amount of dispersant) were kept at base case conditions. As shown in Figure 3.17, M_w increases significantly with the

higher monomer loadings, while particle size increases slightly. As the amount of initiator is kept the same, the increase in M_n (or M_w) can be explained by the increased ratio between monomer ([M]) and initiator ([I]) concentrations. The increased particle size might also be a result of increased solubility of oligomers in the system with higher [M] (higher j_{crit}) and thus a corresponding decreased particle number in the medium.[21]

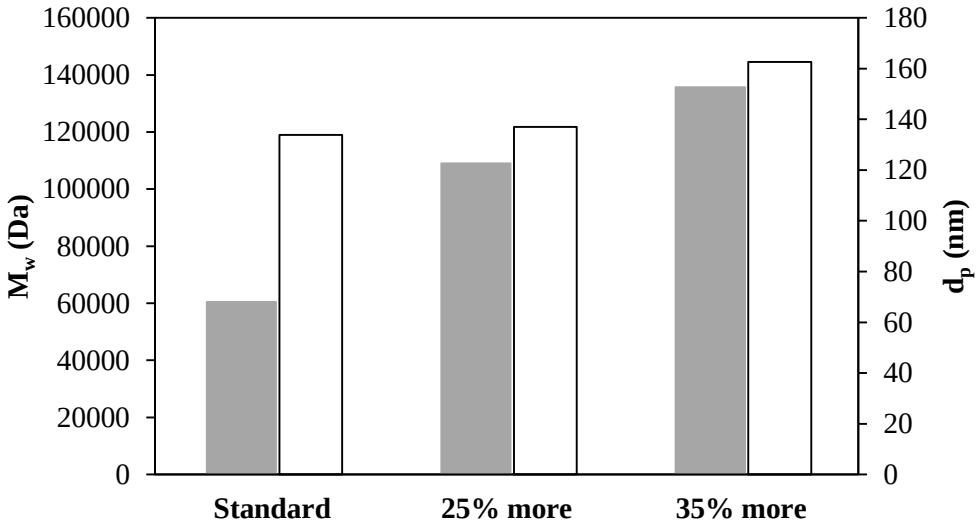

Figure 3.17 Weight-average molecular weight and average particle size of NADs made with higher core amounts: M_w (filled bars) and average particle size (unfilled bars).

The solvent fraction of the standard NAD is a mixture of 70 wt% heptane and 30 wt% xylenes, with the xylenes entering the reactor as solvent for the dispersant. As a final set of investigations, the polarity of the solvent mixture was gradually increased by adding a greater fraction of xylenes to the solvent mixture, with 10 wt%, 25 wt% and 40 wt% of the original (base case) heptane amount replaced by xylenes. Xylenes is a better solvent for the core copolymer p(MMA/MA), as heptane works as a non-solvent. Thus, increasing the xylenes fraction is expected to increase the value of j_{crit} in the system and cause delayed nucleation and a

corresponding increase in particle size, as shown in previous batch studies.[16,17] This concept has been verified by studying the solubility of pMMA, pMA and p(MMA/MA) oligomers in heptane/xylenes mixtures of varying composition in a non-reactive systems, as described in Appendix A.1.1

Under the semibatch conditions used in this study, the relation between the solvent medium and the average particle size seems more complicated, as illustrated in Figure 3.18. Almost the opposite results are seen, as particle size decreases with the increased polarity of the solvent (higher xylenes amount), except for the data collected with the highest xylene fraction. A lowered M_w is also expected as the xylene fraction is increased (more reaction in solution due to higher j_{crit}); however, no consistent variation is seen, with the M_w of the standard NAD lower than that of the NAD made with 10% of the heptane replaced with xylenes (90% heptane shown on the x axis in Figure 3.18).

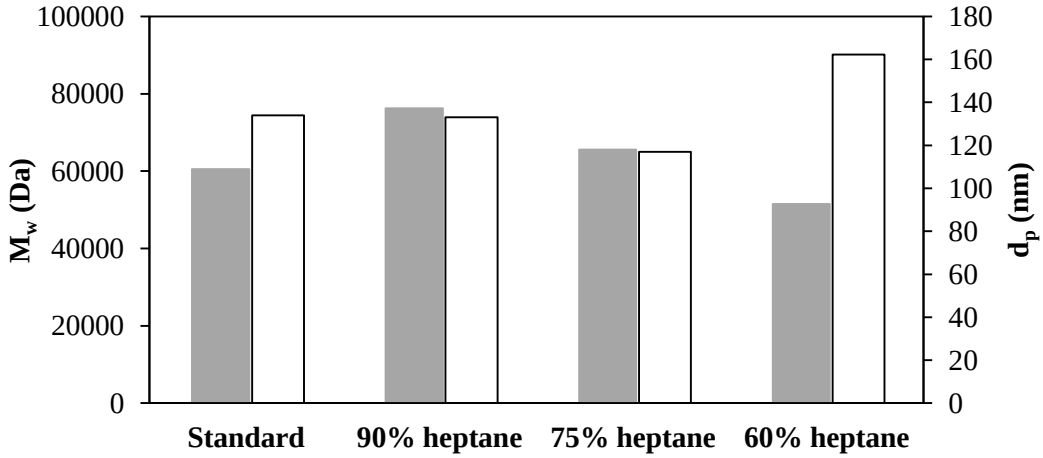

Figure 3.18 Weight-average molecular weight and average particle size of NADs made with different heptane/xylenes compositions: M_w (filled bars) and average particle size (unfilled bars).

3.6 Conclusions

The simplified recipes developed to produce dispersant and dispersion in this work are shown to be an effective way to make stable NAD particles; minimizing the number of monomers used facilitates the study of nucleation described in the following chapter. A reliable SOP for particle size analysis has also been developed, adapted from the standard procedure used by Axalta Coating Systems.

Starting from the simplified recipes, dispersants made with different functional group levels were synthesized and utilized to make NADs. Increasing functionality of the dispersant increases the MW of the corresponding NAD produced, and the fraction of dispersant that reacts with the core during the semibatch dispersion process, as qualitatively observed by examining the SEC traces. However, it is better to control the molar ratio between GMA and MAA to 0.5, as specified in the patent literature; an increased ratio leads to gel formation in NAD product. The same range of NAD particle size is produced with the addition of cross-linking agents (GMA and MAA to the simplified dispersion recipe) in comparison with the commercial NAD, although with a broader dispersity.

The study of reaction conditions suggests a possible approach to tailor particle size and molecular weight of NAD, as well as improve recipe efficiency. Lowering the amount of dispersant added, as well as feeding all of the dispersant with monomer, leads to larger particles and higher M_w, with the same results observed for increased monomer mass in the core. It seems that adding all the dispersant at the start of the batch has only a slight effect on M_w and d_p, and thus this strategy will be further explored in later chapters as a means to simplify the experimental procedure. The effect of solvent composition in the semibatch process on particle size is more complex, and needs to be investigated further.

Although multiple characterization methods have been developed as part of the initial efforts to understand the NAD system, it is clear that additional procedures, such as the measurements of dispersion viscosity and quantification of the unreacted dispersant, are needed. These tests were developed for future investigations. However, from the preliminary work described in this chapter, it is obvious that a significant fraction of dispersant is not effectively used to stabilize the NAD particles, a result that has motivated the investigation of alternative dispersants (macromer), as described in later chapters.

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Chapter 4

Investigating the Effectiveness of Reactive Dispersants in Non-Aqueous Dispersion Polymerization

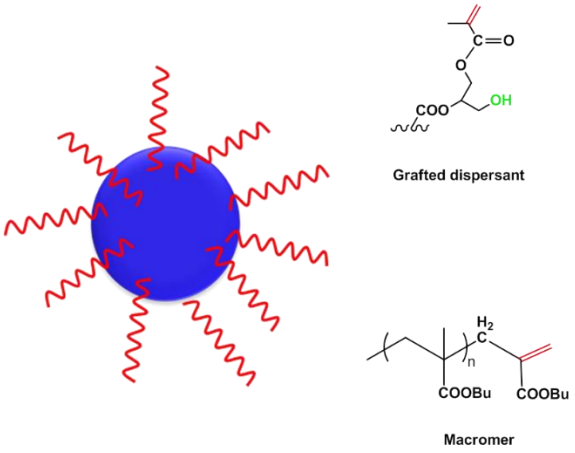
Preface

In this chapter, the performance of vinyl-terminated BMA-based macromers is compared to that of the standard grafted dispersants during the production of NADs with different core compositions. As part of the effort, a new analytical method was developed to quantitatively determine the amount of free dispersant remaining in the continuous phase, as an indication of the performance of dispersant as the steric stabilizer. The MWD of the soluble polymer fraction is compared to that of the original dispersant, providing additional insight into the dispersant effectiveness. In addition, a standard procedure to measure dispersion viscosity was developed.

Most of the content presented in this chapter has been published in the journal *Macromolecular Reaction Engineering* (2016, vol. 10, 71-81). Thus, there is some repetition in the introduction and experimental details sections. The results section (Section 4.3) has been left unchanged from the publication, with additional discussion and related results (not in the publication) added as Section 4.4.

Abstract

Non-aqueous dispersion (NAD) radical polymerization is used to produce poly(acrylic) nanoparticles (<200 nm) at 60 wt% solids content by a starved-feed semibatch process, with steric stabilization provided by a low molecular weight vinyl-functionalized polymeric dispersant. The performance of a vinyl-terminated BMA macromer is compared to that of a BMA based grafted dispersant with vinyl groups attached at random positions along the backbone. The macromer dispersant is incorporated more effectively than the randomly grafted dispersant, a result attributed to the uniform distribution of reactive double bonds across the entire dispersant molar mass distribution, although the effectiveness of the macromer dispersant decreases when methacrylates are components of the NAD recipe.



4.1 Introduction

Non-aqueous dispersion (NAD) polymerization is a technique to produce nanometer-sized polymer particles at high solids content (~60 wt%). These dispersions have been used since the 1960s as a component of solvent-borne automotive coatings formulations, added to prevent crack propagation and control the rheology upon application.[1] Today NADs are also added to hybrid polymer coatings systems in order to reduce solvent content while lowering energy consumption during the curing stage. The nanoparticles are of similar acrylic composition but of much higher molecular weight (MW) than the soluble polymer fraction of the formulation, and become uniformly cross-linked into the final topcoat or clear coat upon application without affecting optical clarity.

In dispersion polymerization, the system is initially homogeneous but becomes heterogeneous as the reaction proceeds, since the continuous phase is a poor solvent for the polymer that is being produced. While there has been limited study of non-aqueous dispersions, much can be learned by examining the literature on particle formation in dispersion polymerizations conducted with common vinyl monomers like methyl methacrylate (MMA) or styrene (ST) in alcohol/water mixtures[2–4] or supercritical carbon dioxide ($scCO_2$).[5,6] Fewer studies have been conducted in aliphatic hydrocarbon solvents such as hexane[7] and dodecane,[8] with shorter carbon chains (lower than butane) shown to be not effective.[9] The solids content in these literature studies is normally at a significantly lower level (<20 wt%) than that used in industrial NAD formulations (50-60 wt%). Polar organic stabilizers with labile hydrogen atoms are often used in alcohol/water dispersions, such as poly(vinyl pyrrolidone), hydroxyl propyl cellulose, poly(acrylic acid), and poly(amic acid).[10–14] These dispersants can become chemically attached to the polymer particles through H-atom abstraction by growing oligomers to form in-situ grafts; a portion of the stabilizer may also be physically adsorbed onto the newly formed particles.[13]

Unlike the homopolymer dispersants in the polar solvent system (alcohol/water), early studies with natural rubber or polybutadiene dispersants in non-aqueous dispersions led to gel formation at high conversions,[1] leading to the utilization of random[15] or block[16] copolymers or macromers[8] as steric stabilizers for non-polar NADs. A commercial macromer, methacryloxypropyl terminated poly(dimethylsiloxane) has been applied to make narrow distributed poly(methyl methacrylate) (pMMA) particles of 0.5-2.0 microns in dodecane[8] and in hexane;[7] however, attachment of the dispersant to the particle surface was low, with only 10-20% of the dispersant added found attached to the particle surface despite the reactive end groups.[8] Poly(12-hydroxystearic acid) (pHS) functionalized with reactive double bonds is also used as a reactive dispersant;[1,17] however, as it is not completely soluble in non-polar solvents,[8] the resultant polymer has also been reacted with MMA to form a comb (pHS-g-pMMA) copolymer in a multi-step synthesis process.[17,18] This dispersant was then used to produce 500-700 nm pMMA particles in dodecane with up to 50 wt% solids content; in this case, it is hypothesized that the dispersant physically, rather than covalently, attaches to the particle surface.[18]

Although the above studies are relevant, the particle sizes are generally larger than those required for coatings applications, with the objective of many of the studies to synthesize micron-sized particles with a very narrow size distribution for applications such as electrophoretic displays,[8] support of biological materials[19] and for chromatographic applications.[20] Thus, the research has little concern for optimizing the usage of the dispersant in the system and for robustly producing dispersions with high polymer content and controlled viscosity, of paramount interest for automotive coating applications. In addition, the literature studies are conducted in batch, rather than the semibatch strategies practiced in industry for composition and temperature control.

In dispersion polymerization for coatings,[1] a typical NAD formulation contains polymer content of 50-60 wt%, with roughly a 1:2 ratio of stabilizer (dispersant) to core polymer, with

particles typically less than 300 nm. The soluble dispersant polymer, also an acrylic polymer but of lower polarity than the NAD core, is produced in a separate batch, sometimes involving multiple steps. Vinyl functionality is introduced to these low MW chains (weight-average molecular weight (M_w) less than 10,000 Da) such that the molecules become covalently attached to the higher MW (M_w greater than 50,000 Da, with cross-linking agents sometimes added) polar chains that precipitate out in the dispersion, thus preventing flocculation and controlling the average size of the polymer particles. It is possible that some of the dispersant also stabilizes by physical adsorption to the particle, and a significant portion of unreacted free dispersant remains in solution.

Despite these differences, there are important common features between academic and industrial dispersion systems. Particle nucleation, which occurs in the early stages of the reaction to control particle number and size, is not well understood. The polymeric dispersant is of critical importance, as it creates a reproducible polymerization system (unlike precipitation polymerization) by providing colloidal stability and helping to control average particle size and size distribution of the polymer produced.[1] Solvent selection is also critical, with particle size and distribution greatly influenced by the composition.[21–23]

In this work, we systematically examine the semibatch non-aqueous dispersion polymerization of methyl methacrylate and methyl acrylate in heptane, using a functionalized low MW poly(butyl methacrylate) dispersant prepared in xylene. Using patent literature as a guide,[24] this simplified recipe is used to produce low viscosity 60 wt% polymer dispersions with average particle size less than 200 nm. Of particular interest is the role of the reactive dispersant, as we contrast the performance of material with randomly-distributed functionality to that of macromers with controlled functionality, as a means to improve the effective utilization of the dispersant.

4.2 Experimental Section

4.2.1 Materials

The monomers, n-butyl methacrylate (BMA, Sigma-Aldrich, 99%), methacrylic acid (MAA, Sigma-Aldrich, 99%), glycidyl methacrylate (GMA, Sigma-Aldrich, 97%), methyl methacrylate (MMA, Sigma-Aldrich, 99%) and methyl acrylate (MA, Sigma-Aldrich, 99%), were used as received. The initiators, t-butyl peracetate (TBPA, Sigma-Aldrich, 50 wt% in mineral spirits) and 2, 2'-azobis-(2-methylbutyronitrile) (Vazo® 67, E. I. du Pont), were also used without any purification. The inhibitor catechol (Sigma-Aldrich, ≥99%) and the amino catalyst, 2-dimethylamino-2-methyl propanol (Sigma-Aldrich, 80 wt% in water), were utilized as received. Solvents used in the study, also without purification, were isopropanol (Sigma-Aldrich, 99.5%), xylene (Sigma-Aldrich, ≥98.5%), p-xylene (Sigma-Aldrich, ≥99), deuterochloroform ($CDCl_3$, Sigma-Aldrich, 99.8 atom% D), heptane (Sigma-Aldrich, ≥99%), and butyl acetate (Sigma-Aldrich, ≥99%).

4.2.2 Preparation of Dispersant Polymer

All polymerizations were carried out in a 1 L semibatch reactor, which has been intensively used in our group.[25,26] The recipe developed for this work is based upon patent literature,[24] with a simplified copolymer formulation used (BMA based material with MAA added for functionality) rather than the 6 monomer system described in the patent. The operating procedure, however, was identical to the patent example, scaled to the 1 L reactor. 178.7 g xylene was added to the reactor and heated up to 138 °C. A mixture consisting of 409.7 g BMA, 9.8 g MAA (3.8 mol% MAA with respect to total monomer), 22.5 g TBPA solution and 67.3 g xylene was pumped to the reactor at constant rate over 240 min and then held for another 30 min; at this point, the conversion of the system is close to complete (> 95%). A mixture of 0.016 g catechol

(to inhibit any further radical polymerization) in 0.18 g isopropanol was added, followed by 8.1 g GMA (a molar ratio of 0.5 relative to MAA) and 0.1 g 2-dimethylamino-2-methyl propanol (amine catalysis to promote reaction of the GMA epoxy group with the MAA carboxyl group). The system was held at reaction temperature for 120 min then cooled to room temperature. The final dispersant contained ~60 wt% BMA-based polymer in xylene solvent. Three versions were produced, with the molar ratio between GMA and MAA set at 0, 0.5, and 1.0.

The BMA macromers, also 60-65 wt% in xylene, were kindly prepared and provided by Dr. Andrew P. Stamegna from Axalta Coating Systems.

4.2.3 Non-Aqueous Dispersion Polymerization

MMA/MA copolymer and MA homopolymer systems were investigated as the core, with the conditions (temperature, addition rates, initiator amount, and ratio of dispersant to monomer) once again based upon patent literature.[24] The reactor was charged with 128.2 g dispersant polymer solution and 130.1 g heptane, then heated to 92 °C; heptane is a non-solvent for the more polar core polymer formed during the reaction, but is a good solvent for the BMA-based dispersant. A pre-mixed solution of 4.3 g butyl acetate and 0.32 g Vazo 67 was added, followed by addition over 210 min of a mixed solution consisting of 139.2 g MMA, 65.8 g MA, 48.7 g heptane, 64.4 g dispersant polymer solution and 2.5 g Vazo 67. The dispersion was held at 92 °C for a further 45 min, followed by addition of a solution of 0.82 g Vazo 67 and 9.8 g butyl acetate over 30 min and a further hold for 60 min. The dispersion was cooled down to room temperature. Samples were taken at regular intervals during the reaction.

4.2.4 Quantification of Free Dispersant

The fraction of dispersant attached to the NAD nanoparticles was quantified by measuring the amount of the soluble polymer that remains in the continuous phase. 2 g of the NAD dispersion was diluted with 5 mL heptane. The mixture was centrifuged at 6000 rpm for 10 min to separate the phases into a clear upper solution and a dense particle-rich layer. The clear liquid was collected, and the amount of polymer in solution was determined by gravimetry, leading to the estimate of w_{inc}, defined as the weight fraction of the incorporated dispersant; further details of this calculation are provided in Appendix A.2. In addition, the soluble polymer recovered was characterized by proton nuclear magnetic resonance (^{1}H NMR) and size exclusive chromatography (SEC).

4.2.5 Characterization

^{1}H NMR was used to qualitatively verify the presence of reactive double bonds on the functionalized dispersant and quantitatively measure the amount of the soluble polymer recovered from the NADs. Spectra were measured using a Bruker Acance-400 MHz spectrometer with automation on dried polymer dissolved in $CDCl_3$.

Polymer MW averages and molar mass distributions (MMDs) were measured for all dispersants, for the soluble polymer recovered from the NADs, and for the complete NAD samples (mixed particle and continuous phases). The SEC analysis of lower MW samples (dispersant and soluble polymer) was done using a Waters 410 differential refractometer (DRI) operated at 35 °C, with THF as eluent at a flow rate of 0.3 mL·min^{-1}. The DRI detector was calibrated by 10 narrow polystyrene (pST) standards with MW from 870 to 355,000 Da. The MMDs for the NAD polymer (higher MW samples) were analyzed by SEC using a Viscotek 270 max separation module with triple detectors. THF was used an eluent at 1.0 mL·min^{-1} at 40 °C. The reported results are based upon pST calibration, without further correction.

Average particle size and size distribution were measured on a Malvern Zeta-Sizer Nano ZS using dynamic light scattering (DLS) with an angle of 173 °at 25 °C in a quartz cuvette. Samples were diluted using a solvent mixture (50 wt% heptane and 50 wt% p-xylene), with the refractive index (1.418) and viscosity (0.562 cP) of the binary solvent mixture calculated via the Lorentz-Lorenz formula[27] and the Grunberg and Nissan equation,[28] respectively. The refractive index of polymer dispersion is 1.59, as provided by Axalta Coating Systems. Viscosities were measured at room temperature using a Brookfield Viscometer with a UL adapter at a rotation rate of 0.5-1.0 rpm.

4.3 Results and Discussion

4.3.1 NAD Synthesis With Grafted Dispersant

Controlling the number of functional vinyl groups per dispersant polymer chain is important to have a soluble and effective stabilizer.[1] Conventional "grafted" dispersants are made by starved-feed free radical polymerization to produce copolymers with carboxyl groups, which then are functionalized through an amine-catalyzed reaction with the epoxy group of glycidyl methacrylate (GMA) to produce a functional unsaturated dispersant, as shown in Figure 4.1a.[24,29] As summarized in Table 4.1, the dispersants synthesized in this study all have the same base composition (M_n of ~4500 Da for an average chain length of 30 monomer units, with 4 mol% MAA for an average of 1.0 MAA units per chain), but have been reacted with differing levels of GMA to vary the level of functionalization of the chain. Assuming quantitative reaction, the average number of double bonds per chain for Dispersant I, Dispersant II and Dispersant II is 0, 0.5 and 1.0, respectively. As described in Appendix A.2.2, the presence of the double bond in the dispersant after the esterification is confirmed by ^{1}H NMR, as has been observed in literature.[30] With half of the carboxyl groups functionalized, Dispersant II is similar to the examples found in

the patent literature;[24] Dispersant I (non-functionalized) and Dispersant III (fully-functionalized) were synthesized to further investigate the role of the functional groups during NAD synthesis.

Table 4.1 pBMA-based grafted dispersants produced with varying GMA to MAA molar ratio.

Sample	GMA/MAA molar ratio	M_n (Da)	M_w (Da)
Dispersant I	0	4300	7500
Dispersant II	0.5	4800	9600
Dispersant III	1.0	4800	9300

The dispersant solutions, consisting of 60 wt% polymer in xylene solution, are stored and used as a reactive component to produce polymeric nanoparticles in non-aqueous dispersion (NAD), also by a starved-feed semibatch process. Figure 4.1b is a schematic of the reaction of the grafted dispersant with the radicals (MMA or MA) in the system during NAD copolymerization. As described in Section 4.2, two thirds of the dispersant is pre-charged to the reactor (along with solvent), and the remaining amount fed with monomer, initiator and additional solvent over a 3.5 h period. The final NAD low viscosity mixture (easily pourable) contains 60 wt% polymer in xylene/heptane solvent, of which 20 wt% of the polymer is the original dispersant, and the remaining 40 wt% is polymer formed by complete conversion of the MA/MMA monomer into polymer particles. The more polar MA/MMA copolymer precipitates out of the non-polar heptane solvent as it is formed, with the nanoparticles stabilized by the reactive dispersant. Images of NAD samples taken in the polymerization period are shown in Figure 4.2. The solution is still clear at 20 min, then turns translucent (40 min) to milky and opaque after 60 min. Nucleation of polymeric particles formed by dispersion polymerization in polar media occurs at the early stages of polymerization,[31] and in batch systems the number of particles remains constant after

nucleation, with newly generated small particles (or polymer chains) swept up by existing particles.[23] Figure 4.3 demonstrates that particle size remained relatively constant in the semibatch system after 120 min; unfortunately, it was difficult to obtain reliable data during the earlier nucleation stage of the reaction. Although the particle size and concentration remains constant, the total number of particles increases over the feeding period, likely due to the concurrent addition of dispersant solution with monomer (see Appendix A.2.6 and A.2.7).

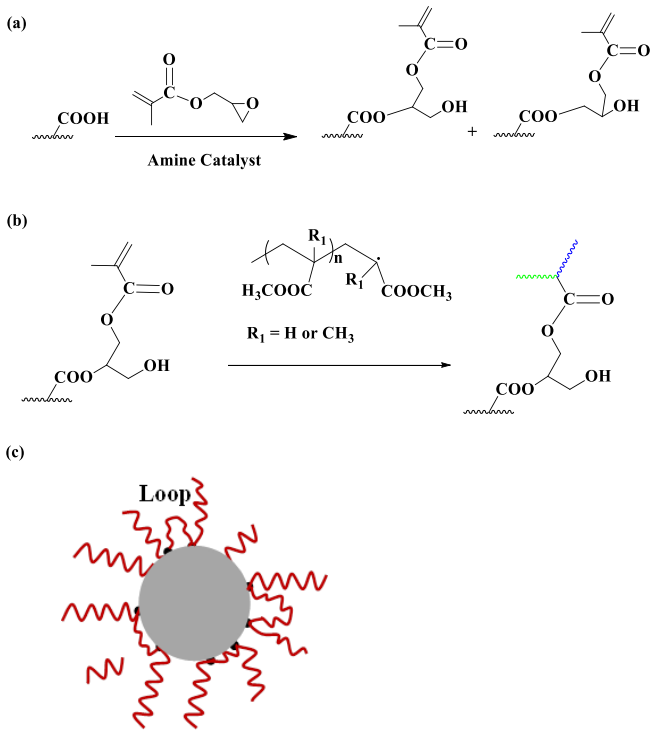


Figure 4.1 Schematic of reactions involved in the synthesis of NAD prepared with grafted dispersant: (a) reaction between GMA and MAA units to introduce vinyl functionality to the polymer dispersant; (b) addition of the vinyl-functionalized dispersant to MMA or MA radicals present during NAD synthesis; (c) proposed attachment of dispersant to the particle surface, with multiple functionalities per chain leading to the potential of multiple surface attachments, loop formations and cross-links.

Varying the level of functionalization on the grafted dispersant helps to provide a clearer picture of its role during particle formation. As seen in Figure 4.2, the formation of particles in NAD I is delayed, as there are no double bonds by which Dispersant I can become covalently incorporated to the MA/MMA copolymer particles. The influence of the level of functionalization on the properties of the final NAD product is summarized in Table 4.2. The amount of Dispersant I attached (or physically adsorbed) to the particles is only 13%, as quantified by performing gravimetry on the continuous phase after destabilizing the dispersion to separate out the particles. Introduction of the reactive double bonds to the polymer increases the fraction incorporated to 32% for NAD II (made with Dispersant II) and 44% for NAD III (made with Dispersant III). The effect on dispersant incorporation on average particle size is clear, as seen by the corresponding decrease from 237 (NAD I) to 162 (NAD II) to 147 nm (NAD III).

Table 4.2 Properties of NAD polymer synthesized using grafted dispersants with varying double bond content (GMA/MAA molar ratios, see Table 4.1).

Sample	GMA/MAA molar ratio	M_n (Da)	M_w (Da)	w_{inc} [b)]	d_p (nm)[c)]
NAD I	0.0	12100	60300	0.131	237
NAD II	0.5	12300	92700	0.320	162
NAD III	1.0	10500[a)]	110300[a)]	0.440	147

a) Sample collected at 285 min; gel formed for sample at 390 min (final product).
b) w_{inc} is the weight fraction of dispersant that is attached to the particle, as determined from analysis of the amount of polymer remaining in solution.
c) d_p is the average particle size, as measured by DLS.

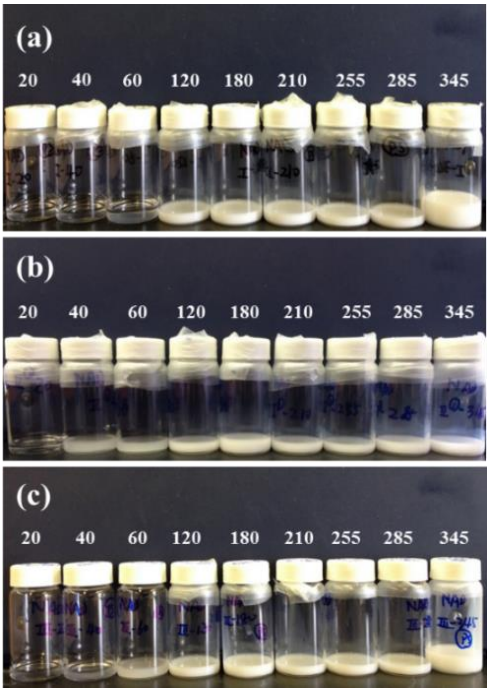


Figure 4.2 Photographs of non-aqueous dispersion samples taken during the reaction period, with sample time (min) indicated above the individual vials: (a) NAD I; (b) NAD II; (c) NAD III.

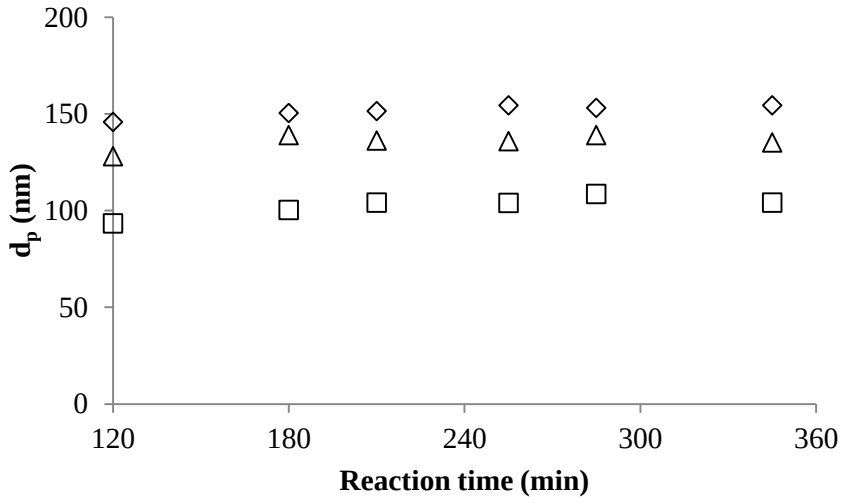


Figure 4.3 The evolution of particle size during the semibatch production of NAD II (diamond), NAD B-M2 (square), and NAD B-M5 (triangle).

These results suggest that increased functionalization is a viable means to decrease particle size while also increasing the utilization of the dispersant. (Other approaches, such as recipe modifications are being studied, but will not be discussed in this publication.) However, there is a practical limitation to this approach. While starved-feed reactor operation provides excellent control of the average number of MAA units incorporated per dispersant chain (and thus double bonds per chain via epoxidation), the stochastic nature of radical polymerization means that even under perfect control of overall copolymer composition, a significant fraction of the polymer chains produced contains no functionality. A recent simulation study demonstrates that most of the chains without functionality are, not surprisingly, at the low MW side of the distribution, and that many of the chains on the high MW side of the distribution contain multiple functional groups per chain.[32] This stochastic variability is quite important when producing low MW functional polymers: the simulation study indicated that for a number-average chain length of 20 and a single functional group per chain (on average), only a quarter of the chains produced have the desired functionality of one unit per polymer molecule, with close to half of the chains produced containing no functional groups.

Our experimental findings illustrate the importance of functional group distribution in the dispersants. Figure 4.4 compares the molar mass distributions (MMDs) of the NAD product with those of the dispersants used in the reaction. The MMDs are bimodal, with the low-MW mode overlapping the MMDs of the original dispersant, indicating that a high fraction of the dispersant has not reacted. It can also be seen that the NAD II and NAD III polymers have an observable increase of material in the high MW tail, as also reflected in the weight-average (M_w) values summarized in Table 4.2. Note that it was not possible to measure the MMD of the final NAD III sample, as the polymer did not fully dissolve in THF; thus the MMD shown (and M_w reported) is from a sample collected earlier in the reaction. We hypothesize that NAD III is partially cross-linked, due to the reaction of multiple double bonds located on the higher MW Dispersant III

chains, as illustrated schematically in Figure 4.1c. The chemical attachment of dispersant to the particle surface is dependent on the number and location of the functional groups, with more than one attachment likely formed for the higher MW dispersant. Although the formation of cross-linking may not affect the product application (some core systems are cross-linked by design[24]), the efficacy of the dispersant may be lessened due to the loops formed with multiple attachments of the chain to the particle surface.[33]

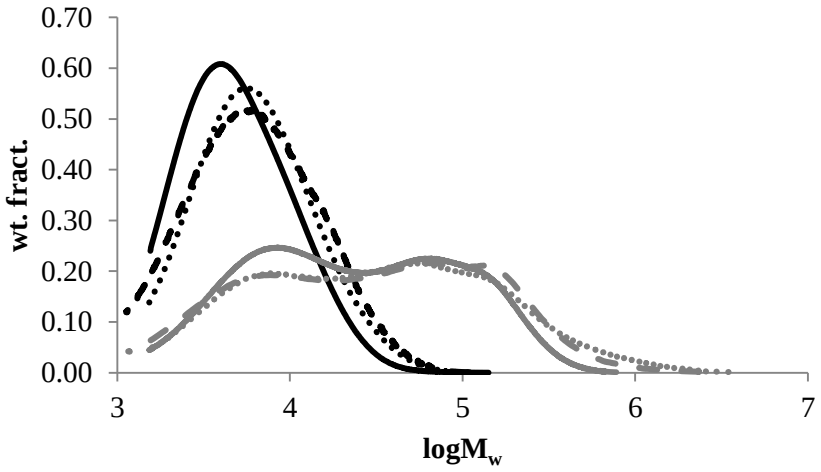


Figure 4.4 Polymer MMDs of dispersants (black lines) and the corresponding product produced by non-aqueous dispersion (NAD) polymerization (grey lines): Dispersant I/NAD I (solid lines), Dispersant II/NAD II (dashed lines) and Dispersant III/NAD III (dotted lines).

The soluble polymer that remains in the continuous phase has been separated out from the NAD product for further analysis. NMR analysis (see Appendix A.2.3), shows that this material is predominantly (>95 wt%) the original BMA-based dispersant, although some MMA/MA soluble copolymer is also found. The proton signal from the dispersant double bonds is no longer observable by NMR, suggesting that the chains that remain in solution are largely

unreactive. This finding can also be inferred by comparing the MMDs of the soluble polymer to that of the original dispersant. The distributions from NAD II and NAD III soluble fractions are shifted to lower MW (loss of higher MW tail) compared to Dispersant II and Dispersant III, respectively, as observed in Figure 4.5b-c. In contrast, the MMD of the soluble polymer from NAD I is exactly the same as the non-functionalized Dispersant I (Figure 4.5a).

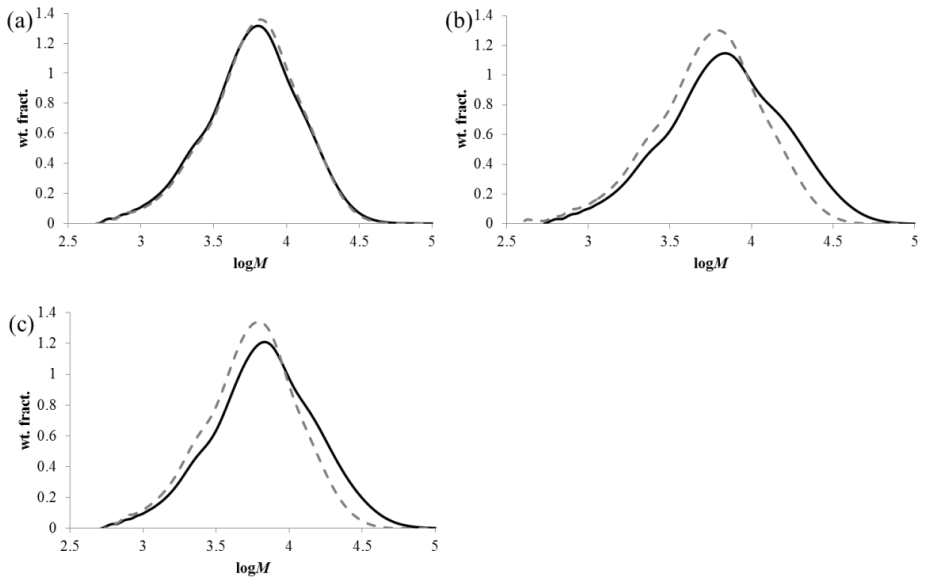


Figure 4.5 MMDs of polymer dispersants (solid lines) and soluble polymer fraction isolated from NADs (dashed line): (a) Dispersant I/NAD I; (b) Dispersant II/NAD II; (c) Dispersant III/NAD III.

These results provide a strong indication of the uneven distribution of vinyl groups in the grafted dispersant produced by free radical polymerization. The higher MW chains contain a greater number of the reactive double bonds, and thus are preferentially removed from solution by reaction with the NAD core polymer. Thus, while increasing the double-bond content of the dispersant leads to smaller particles and an increased utilization of the dispersant, it can also lead to the formation of cross-linked polymer due to the higher probability of having multiple

functionalities per chain. The lower MW chains, more likely to contain no functionality, are not available for reaction and thus are less effective at stabilizing the particles. While the dispersant system can form stable NAD products, there is opportunity for improvement.

4.3.2 NAD Synthesis with Macromer Dispersant

We hypothesized that the efficacy of the dispersant can be increased if it is possible to ensure that every chain contains exactly one reactive double bond, and if that bond is located at the end of the chain such that the stabilizer molecule extends out from the particle surface after being incorporated (Figure 4.6c). Thus a series of butyl methacrylate macromers have been synthesized by cobalt chain transfer (CCT) polymerization (Figure 4.6a) and tested as potential dispersants for NAD polymerization. CCT is a well-understood technique to produce low molecular weight (MW) polymer chains at relatively low temperatures using ppm amounts of catalytic chain transfer agent without incorporation of the transfer agent into the macromolecules formed. Under well-chosen conditions, nearly all of the polymer chains contain an unsaturated bond at the chain end, such that these polymers can be used as macromers in subsequent polymerization.[34,35] The macromers used in this work were prepared as 60-65 wt% pBMA solution in xylene, so as to provide a direct comparison to the grafted dispersant. As summarized in Table 4.3, a range of chain lengths were studied, with the SEC-measured number-average MW value confirmed by NMR analysis (see Appendix A.2.4).

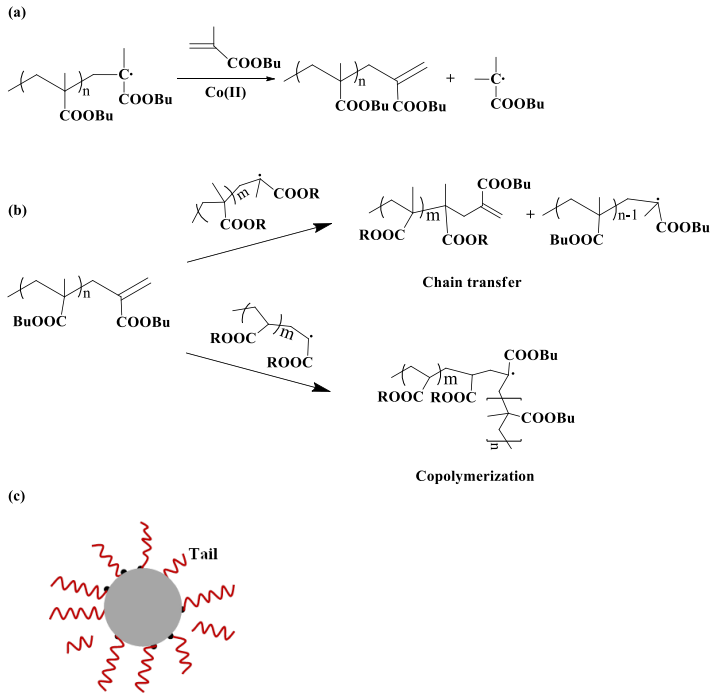


Figure 4.6 Schematic of reactions involved in the synthesis of NAD prepared with macromer dispersant: (a) Macromer synthesis by cobalt chain transfer polymerization; (b) macromer reaction with methyl methacrylate radical (chain transfer) and methyl acrylate radical (copolymerization); (c) proposed attachment of macromer to the particle surface, with a single attachment formed at the macromere chain end.

A series of NAD polymerizations were conducted using these macromer dispersants in place of the grafted dispersants for the same MMA/MA NAD core recipe, with results summarized in Table 4.3. Compared to the NAD particles produced with grafted dispersant (150-160 nm), the NAD particles produced with the macromers are smaller, with an average d_p as low as 100 nm seen. As shown in Figure 4.7a-b, the particles are not evident until the 60 min sample is collected, in contrast to the situation with grafted dispersant (Figure 4.2). The samples at this point still have a bluish tinge, indicative of the smaller particles in the system.

Table 4.3 Properties of butyl methacrylate macromers (M1 through M6) and corresponding NAD copolymer (NAD B-M1 through NAD B-M6) synthesized with macromer dispersants.

Sample	Macromer MWs		NAD Properties			
	M_n (Da)	M_w (Da)	M_n (Da)	M_w (Da)	w_{inc} [a)]	d_p (nm) [b)]
NAD B-M1	5300	9100	12500	38300	0.400	100
NAD B-M2	5600	9200	12200	42900	0.414	104
NAD B-M3	5700	9600	12000	43900	0.405	118
NAD B-M4	6300	11000	12800	44100	0.399	127
NAD B-M5	7100	12000	14100	52700	0.357	135
NAD B-M6	8300	15000	14600	61300	0.344	169

a) w_{inc} is the weight fraction of dispersant that is attached to the particle, as determined from analysis of the amount of polymer remaining in solution.
b) d_p is the average particle size, as measured by DLS.

As shown in Figure 4.8, there is a direct correlation between particle size and macromer M_n; the lower-MW M1-M3 dispersants have a higher double bond content per unit mass, and thus are incorporated more readily into the growing MMA/MA copolymer chains. As the MW values of the grafted and macromer dispersants are similar, it can be concluded that the improved stabilization is due to the even distribution of the double bonds (one per chain) among the macromer molecules compared to the grafted dispersant. Moreover, as the double bond is located at the end of the chain, we hypothesize that the stabilizer chains attached to the NAD particles extend out in solution (Figure 4.6c), in contrast to the attachment of the grafted dispersant (with randomly distributed double bonds) attached to the NAD particles (Figure 4.1c).

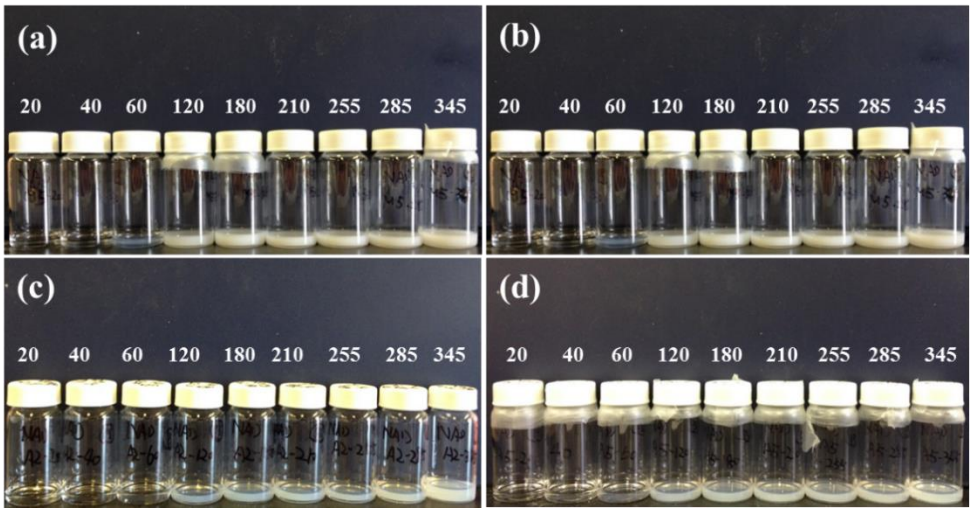


Figure 4.7 Photographs of NAD samples taken during the reaction period, with sample time (min) indicated above the individual vials: (a) NAD copolymer synthesized with M2; (b) NAD copolymer synthesized with M5; (c) NAD acrylate homopolymer synthesized with M2; (d) NAD acrylate homopolymer synthesized with M5.

Despite the decrease in particle size, the fraction of the macromer dispersant that is incorporated (or adsorbed) onto the NAD particles is 30-42 wt%, with the majority of the dispersant remaining in the continuous phase. This result was surprising, as it was expected that the even distribution of double bonds in the macromer would lead to improved dispersant incorporation compared to the grafted dispersant. In addition, as summarized in Table 4.3, the average MWs of the NAD polymer produced are significantly lower (M_w values of 4-6×10^3 Da) than those of the polymer produced with the grafted dispersants (Table 4.2); as shown in Figure 4.9, it was found that the average MW of the polymer produced decreased as the MW of the macromer dispersant is decreased.

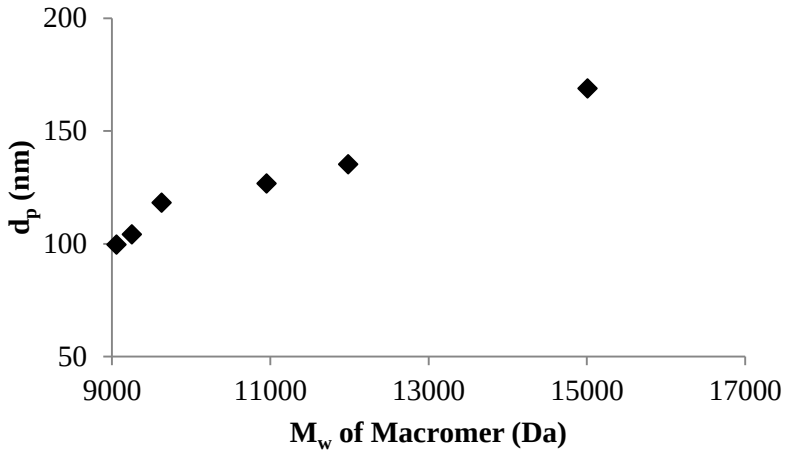


Figure 4.8 Average particle size produced by NAD MMA/MA copolymerization as a function of the weight-average MW of the macromer used as dispersant.

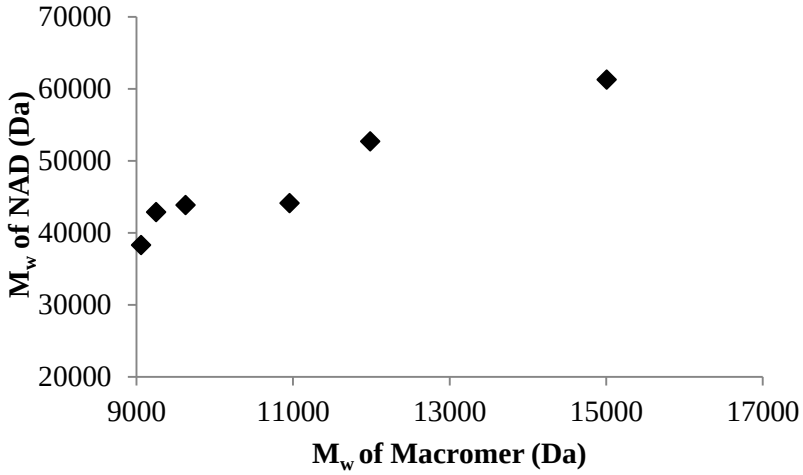


Figure 4.9 Weight-average MW of polymer produced by NAD MMA/MA copolymerization as a function of the weight-average MW of the macromer used as dispersant.

As shown in Figure 4.10, the MMDs of the NAD polymer remain bimodal, with the lower MW peak corresponding to the MMD of the macromers used as dispersants. The soluble polymer recovered from the reactions was confirmed to be predominantly (>95 wt%) unreacted

dispersant that, according to NMR analysis, contained reactive double bonds (see Appendix A.2.5). In addition, the MMD of the soluble polymer fraction was found to overlay the distribution of the original macromer within experimental error, as shown for M2 and M5 in Figure 4.11. (MMD plots for the complete set of macromer, NAD, and soluble polymers samples followed the same trends as those shown in Figures 4.10 and 4.11.)

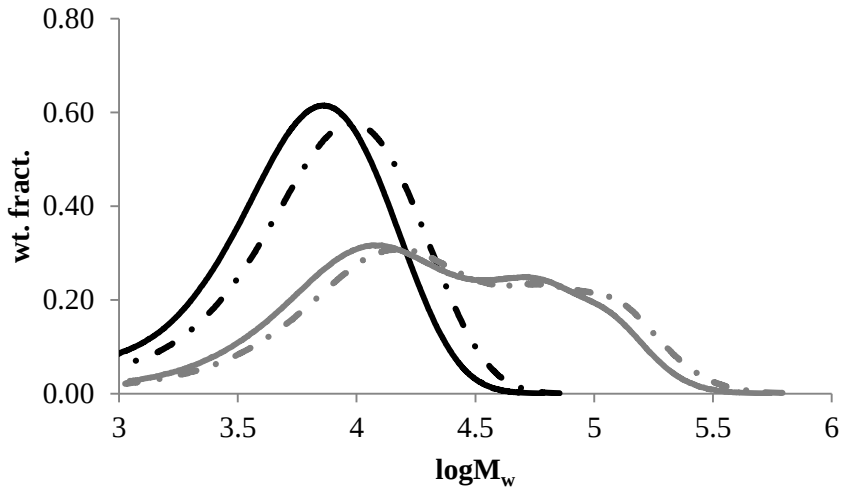


Figure 4.10 Polymer MMDs of macromer dispersants (black lines) and the corresponding product produced by non-aqueous MMA/MA dispersion copolymerization (grey lines) for M2/NAD B-M2 (solid lines) and M5/NAD B-M5 (dot-dash lines).

All of these results indicate that, although complete conversion of the MMA and MA monomers are achieved, the "conversion" (incorporation) of the macromer during NAD formation is significantly lower. This result can be attributed to the lower reactivity of macromers: while the double bond of the grafted dispersant is part of an ester moiety along the chain (Figure 4.1a), the double bond of the macromer is at the terminus, with the polymer chain replacing the CH_3 group of a methacrylate (Figure 4.6a). It has been documented that this type of macromer does not homopolymerize or copolymerize with methacrylates because of the competing β-

scission (chain-transfer) reaction.[36] However, copolymerization of macromer with acrylates readily occurs, such that the macromer is incorporated into the chain as a graft.[36] Both reactions must occur for the methacrylate/acrylate recipe used in this work, as shown in Figure 4.5b: incorporation as a stabilizing graft when reacting with an MA radical, and acting as a chain transfer agent (hence reducing polymer MW) when interacting with an MMA radical.

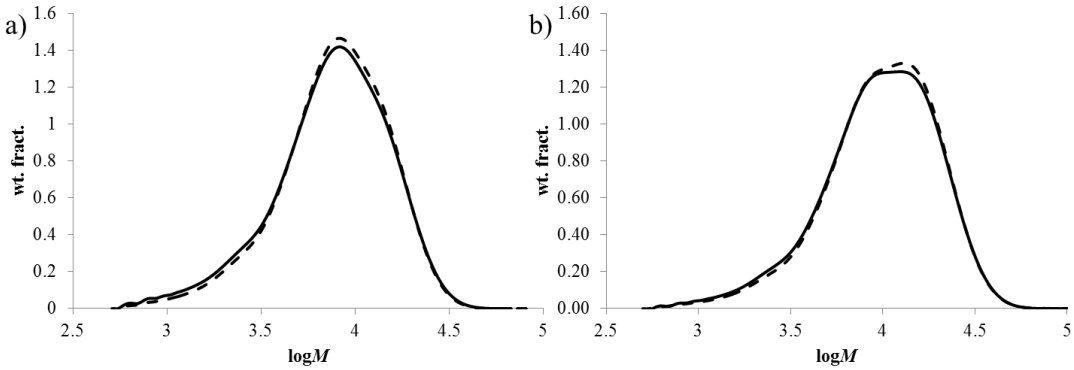


Figure 4.11 MMDs of polymer dispersants (solid lines) and soluble polymer fraction isolated from NADs (dashed line): a) M2 and NAD B-M2; b) M5 and NAD B-M5.

4.3.3 Grafted versus Macromer Dispersant (Acrylate Homopolymer Core)

To further explore the replacement of grafted dispersant with macromer, the performance of Dispersant II was compared to two of the macromers (M2 and M5) for NAD produced using only methyl acrylate as the core. According to the mechanisms discussed above, this should eliminate the chain-transfer reaction that occurs between macromer and methacrylate radicals (no longer present in the system), and thus increase dispersant efficiency.

Table 4.4 Comparison of the properties of NADs with MMA/MA copolymer core and MA only core, synthesized using both grafted dispersant and macromer.

Dispersant	Core	Sample	M_n (Da)	M_w (Da)	w_{inc} [a)]	d_p (nm) [b)]	η (cP)
Grafted	MMA/MA	NAD II	12300	92700	0.32	162	85
(Disp II)	MA only	NAD A-II	11200	86800	0.46	109	236
M2	MMA/MA	NAD B-M2	12200	42900	0.41	104	154
	MA only	NAD A-M2	16000	81500	0.61	70	199
M5	MMA/MA	NAD B-M5	14100	52700	0.36	135	117
	MA only	NAD A-M5	16200	71100	0.59	83	874

a) w_{inc} is the weight fraction of dispersant that is attached to the particle, as determined from analysis of the amount of polymer remaining in solution.
b) d_p is the average particle size, as measured by DLS.

Pictures taken for NAD A-M2 and NAD A-M5 are shown in Figure 4.7c and 4.7d, with the bluish tingle still seen at 120 min indicating a formation of even smaller particles. The results of these experiments are summarized in Table 4.4, which also includes a summary of MMA/MA NAD produced with the same three dispersants. There are several key points demonstrated by these results. First of all, it is seen that while the MW averages are the same for the MA homopolymer and the MMA/MA NAD produced with the grafted dispersant, there is a significant difference for the reactions run with macromer as dispersant. This result is consistent with the hypothesis that the macromer acts as a chain transfer agent rather than as a comonomer with methacrylate radicals and copolymerizes only with acrylate.[36] Thus, the incorporation of the macromer to the acrylate homopolymer core is higher, up to 60%, compared to the 30-42% incorporation when MMA is a component in the recipe. With the increased effectiveness of the dispersant, the average particle size decreases to 70 nm for M2 and 83 nm for M5; the smaller particle size produced with M2 is due to the higher concentration of double bonds (lower M_n)

compared to M5 for the same mass of dispersant added. It is interesting to note that a higher portion of the grafted dispersant is also incorporated with the core for the acrylate homopolymer (with smaller particle size) compared to the copolymer system. This result is not fully understood but may be related to the higher polarity of MA compared to MMA. There is also a small increase in the viscosity of NADs prepared with the MA only core compared to the copolymerization. While undoubtedly related to particle size, the increase in viscosity is larger with M5 compared to the other dispersants. However, in all cases, the NAD produced is stable and pourable. What is clear is that the uneven distributed vinyl group among Dispersant II makes it less efficient than M2, even for the base case methacrylate/acrylate recipe. Although the two polymers have similar MWs (see Table 4.1 and 4.3), M2 has one double bond per chain, while Dispersant II has an average of 0.5 double bonds per chain, with a broad distribution of these double bonds across the MMD.

4.4 Additional Results and Discussions

4.4.1 The Comparison between the Old and New sets of NAD Made with Grafted Dispersant

The set of experiments (grafted dispersant and the corresponding NAD produced) described in Section 4.3.1 repeats those from the previous chapter, with additional characterization performed. The experiments were also performed using different batches of dispersants; however, the deviation on dispersant M_w is small (7%). It is difficult to compare the M_w values of the resulting dispersions, as the Waters SEC setup (better for low MW polymers) was used in the previous chapter, while the Viscotek SEC equipment was employed in this chapter. The average particle sizes between the two sets of experiments were in good agreement, as the biggest difference noticed for NAD I (200 nm and 237 nm for the old and new batches, respectively), indicating the reproducibility of the experiments.

4.4.2 NADs made with the Complete Six Macromers

Analysis of the complete set of MA homopolymer NADs prepared with the six different macromers provides some additional insight. As shown in Figure 4.12, the molecular weight of macromer has little impact on the NAD M_w values, in contrast to what was seen for the MMA/MA copolymer (see Figure 4.9). This result is consistent with the absence of β-scission, which also leads to more effective incorporation of the dispersant, as demonstrated in Figure 4.13: better incorporation of dispersant is found to incorporate with the pMA core (0.52-0.64) compared to the MMA/MA copolymer core (0.3-0.42). As shown in Figure 4.12, there is a gradual increase in average particle diameter with the pMA core, from 70 nm to 100 nm, with increasing molecular weight of the macromer dispersant due to the decreased concentration of double bonds in the system, as the same trend seen for dispersions made with MMA/MA copolymer (see Figure 4.8).

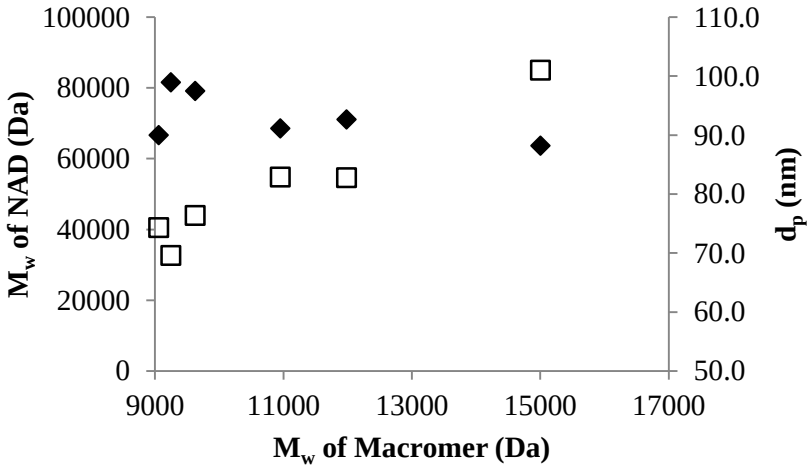


Figure 4.12 Weight-average molecular weight (closed diamond symbols, primary y axis) and average particle size (open square symbols, secondary y axis) of NAD made with MA homopolymer core as a function of weight-average molecular weight of macromer.

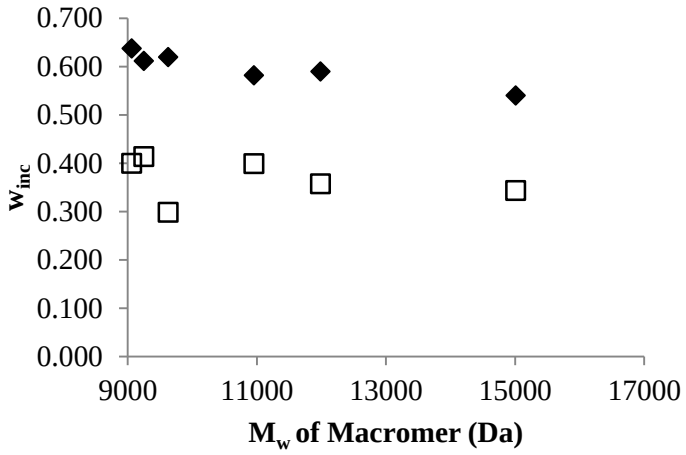


Figure 4.13 Incorporated amount of dispersant with the core in NAD MMA/MA copolymer (open square symbols) and NAD MA homopolymer (closed diamond symbols) as a function of weight-average molecular weight of macromer.

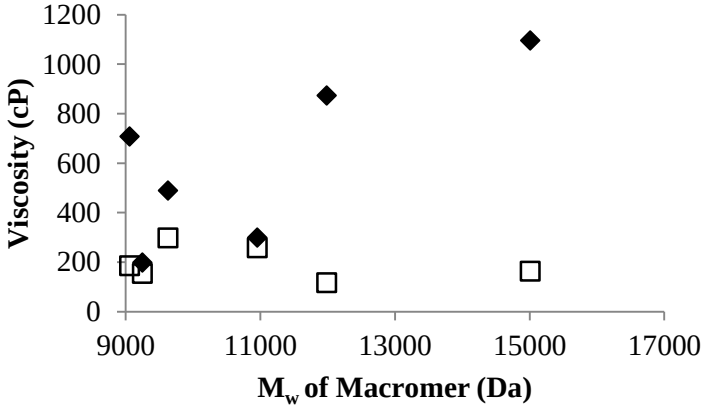


Figure 4.14 Viscosity of NAD made with MMA/MA copolymer (square symbols) and MA homopolymer (diamond symbols) as a function of weight-average molecular weight of macromer.

Figure 4.14 shows that dispersion viscosity remains low (less than 1200 cP) in all cases, with lowered values generally seen for NAD made with MMA/MA copolymer, likely due to their

larger size (probably lower volume fraction) compared to the pMA homopolymer samples under the same given weight fraction.[37]

4.5 Conclusion

NAD products with high solids content (~60 wt%) and small particle size (<200 nm) were produced via starved-feed semibatch polymerization employing two types of reactive polymeric low-MW pBMA-based dispersants. The grafted dispersant was synthesized with the vinyl groups randomly distributed along the backbone, with many low MW chains unfunctionalized. Thus, the effectiveness of the dispersant, as characterized by the fraction incorporated to the particles and average particle size, is lower than that of the (vinyl-terminated) macromers synthesized by BMA polymerization in the presence of a cobalt chain transfer agent. Although the efficacy of the grafted dispersant could be improved by increasing the average double-bond content per chain, the presence of multiple functional groups per chain led to cross-linked cores in the NAD system. Thus, it can be concluded that the macromers provide more efficient stabilization than the grafted dispersant, with the lowest MW macromers (M_n of 5000-6000 Da) most effective due to the higher double-bond content per unit mass.

In the presence of MMA (MMA/MA copolymer core), lower efficacy was found for both types of dispersants compared to NAD produced with an MA homopolymer core, regardless of the different chain length of macromer applied. With macromer dispersant, the standard recipe produced particles of <100 nm in size, with up to 60 wt% of the dispersant incorporated into the particle phase. The improved effectiveness is hypothesized to be partly due to the increased polarity of MA. However, the chain transfer reaction that occurs with methacrylate radicals is eliminated in the acrylate homopolymerization system, thus increasing the effectiveness of macromer as a dispersant and increasing the MW of the NAD polymer. Evaluating the

effectiveness of macromer as dispersant for more complex multi-monomer recipes, as well as examining the influence of dispersant feeding profile on its performance are discussed in the followed chapter.

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Chapter 5

The Influence of Core Composition and Reaction Conditions on NAD Polymerization

5.1 Introduction

In industrial non-aqueous dispersion polymerization, the core composition of the acrylic colloids is varied to match with other components of the overall coating formulation, as well as to increase the overall polymer levels (reduced solvent) in the formulation. The core introduces additional functional groups and influences physical properties, such as providing an increased glass transition temperature, reduced haziness and lowered curing temperature.[1] The dispersion can be mixed with other additives (pigments, screeners and cross-linkers for instance) to improve the post-polymerization consumption.

Core complexity is gradually built up from the acrylate-only homopolymer to a five-monomer copolymer core for NAD systems in this chapter, using both grafted dispersant and two different molecular weight BMA macromers. In addition, a new feeding strategy for the macromer dispersant is investigated, as well as the impact of lowering the dispersant amount.

5.2 Experimental

A 0.6 L glass reactor was utilized to conduct all the experiments in this chapter. The portion of each ingredient has been scaled down to fit this smaller reactor, with the ratio of dispersant, monomers, solvents and initiator kept the same as described in the previous chapter (see Section 3.2.2). All chemicals were purchased from the same companies as mentioned in Chapter 3, with grafted standard Dispersant II prepared according to the recipe specified in

Section 3.2.2. The two different M_w vinyl-terminated butyl methacrylate macromer dispersants (M2 and M6, described in Chapter 4) were kindly provided by Axalta Coating Systems.

The mass of dispersant solution, Vazo® 67, heptane, butyl acetate and monomers was kept the same for all recipes; however, the monomer composition was varied. As listed in Table 5.1, the different NAD core compositions included the addition of 5.8 wt% cross-linker (GMA and MAA), 10 wt% ST and 10 wt% HEA to the MA based recipe. After studying the influence of each of these additions individually, they were combined. The nomenclature for the set of experiments is NAD M-N, where M is the core recipe ("A" = acrylate homopolymer, "AS" = acrylate/styrene copolymer, "AX" = cross-linked acrylate system, "AHX" = cross-linked acrylate with HEA and "AHSX" = cross-linked acrylate with HEA and ST), and N represents the dispersants (Dispersant II, M2 and M6 with MWs summarized in Table 5.2) utilized to make the corresponding NADs.

Table 5.1 Core compositions explored for NADs prepared with grafted and macromer dispersants[a)]

Sample	MA	GMA	MAA	ST	HEA
A-N	100	-	-	-	-
AS-N	90	-	-	10	-
AX-N	94.2	1.6	4.2	-	-
AHX-N	84.2	1.6	4.2	-	10
AHSX-N	74.2	1.6	4.2	10	10

a) The values are based on the fractions of each monomer in the core as wt%.

Table 5.2 Molecular weights of grafted and macromer dispersants

Dispersant	M_n (Da)	M_w (Da)
Dispersant II	4600	9200
M2	5600	9200
M6	8300	15000

The experimental variations utilized for the study of reaction conditions are described at the beginning of each corresponding section of the discussions. Characterization of molecular weight, incorporated amount of dispersant, average particle size and viscosity was conducted via size exclusive chromatography (SEC), proton nuclear magnetic resonance (^{1}H NMR), Malvern Zeta-Sizer Nano ZS and Brookfield Viscometer, respectively, as described in Section 4.2.5.

5.3 Results and Discussions

Non-aqueous dispersions of acrylic nanoparticles studied in this thesis are just one ingredient of commercial coating formulations with other solvents, soluble polymers and additives often added to achieve different physical properties, such as weather-resistance and rheology control. Thus the core is normally composed of multiple monomers to match the requirements for the further application. MMA increases glass transition temperature; cross-linkers (GMA and MAA) make the core insoluble; HEA introduces functional hydroxyl groups; and ST is added to adjust the refractive index. All aforementioned monomers are utilized in commercial NAD recipes outlined in the patent examples.[1] Thus, it is worth the effort to expand our simplified core composition to multi-monomer system, especially in combination with the macromer dispersants that are studied in this thesis.

The other aspect presented in this section is the modification of the feeding strategy and the reduction of the amount of dispersant utilized, in order to explore whether the simplified reaction operations can be used without losing the features (small particle size and low viscosity) of the NAD products.

5.3.1 NAD Prepared with Grafted Dispersant and Macromer with Complex Core

In order to better understand the new sets of results from the core compositions, some of the previous observations from Chapter 4 for the MA-only study are included. It is known that macromer with a higher vinyl group concentration (lower chain length) exhibits better efficacy for the same mass of dispersant. Thus, M2 (a lower M_n vinyl-terminated macromer with the best performance) is chosen as well as M6 (a higher M_n macromer) for comparison in this study, with results compared to our standard grafted Dispersant II. With three dispersants and five different compositions, a total of 15 reactions are discussed. While these experiments were conducted without replicates, the reproducibility (when checked) was similar to that described in the previous chapters and Section 5.3.3. The focus is on the properties of the final NAD solution, as the trends with reaction time are quite similar with those presented in the previous chapters.

The previous chapter compared M_w of NADs made with an MA core to an MMA/MA copolymer core. With the additional experiments conducted in this section, the effect of adding styrene to the MA system is observed (all other compositions used cross-linker). As plotted in Figure 5.1, the values of M_w obtained for NADs made with MA only in the core are consistently higher for all three dispersants compared to the values measured for NADs made with MA/ST copolymer. As previously discussed, a growing chain of macromer can copolymerize with acrylate or undergo β-scission with methacrylate monomer, leading to the production of higher MW copolymers formed with the MA only core.[2,3] Relative rates of addition and β-scission of the

macromer radical reacted with a styrene monomer are less clear. As reported by Cacioli et al.,[4] the MW of graft copolymer formed with MMA-type macromer (short chain length oligomer) and ST was significant lower than that of ST homopolymer under the identical reaction conditions, a result likely due to the formation of sterically hindered radicals which may be less reactive for further monomer addition; a schematic of the sterically hindered free radical in our case is depicted in Figure 5.2. In addition, it is reported by Hamzehlou et al.[5] that the MW of acrylate polymer is reduced when ST is added to the recipe during solution polymerization due to the slower polymerization rate. While both factors can be applied to explain the lower M_w seen when using the macromer dispersants, the lowering of M_w for NAD AS-II as compared to NAD A-II (grafted dispersant) is likely due to the effect of ST on the overall polymerization rate.

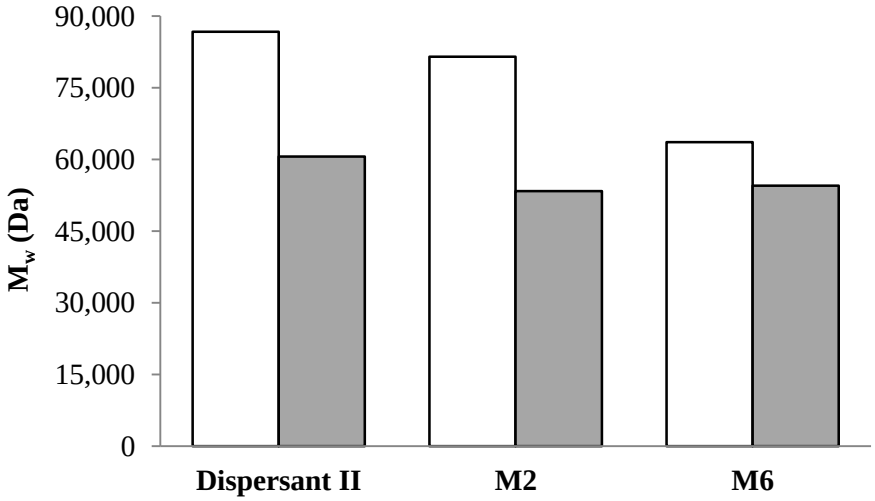

Figure 5.1 Weight-average molecular weight of NADs made with different core compositions: MA homopolymer (unfilled bars) and MA/ST core (filled bars).

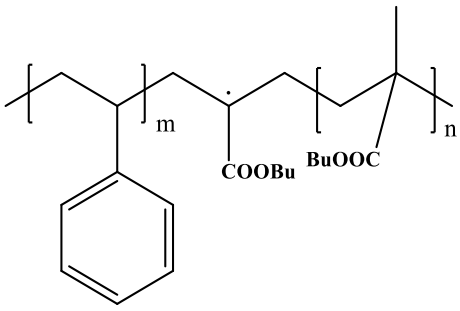

Figure 5.2 Schematic of the sterically hindered radical formed during the copolymerization of BMA macromer and styrene.

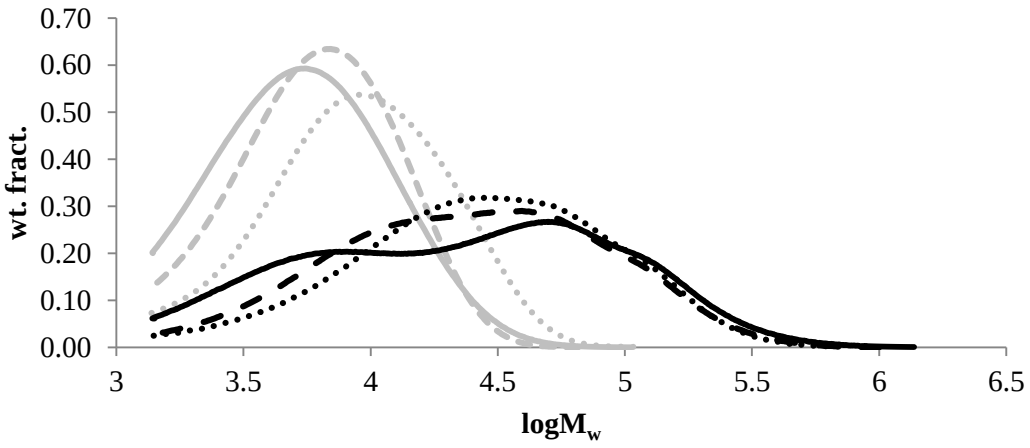

Figure 5.3 MWDs of Dispersants and NADs: Dispersant II (grey solid line) and NAD AS-II (black solid line), M2 (grey dashed line) and NAD AS-M2 (black dashed line), and M6 (grey dotted line) and NAD AS-M6 (black dotted line).

The MWDs of the three dispersants are compared to those of the NAD AS products in Figure 5.3. The bimodal distribution seen for NAD AS-II is similar to that reported for NAD II (with MMA/MA core) in Chapter 4. MWDs of NAD AS-M2 and AS-M6 are similar to what were seen for NAD A-M2 and A-M6 (see Appendix A.2.8), but different from the bimodal plots obtained for NAD B-M2 and B-M5 (Section 4.3.2), as broad featureless distributions (without

two distinct peaks) are observed. This may further support the hypothesis that the sterically hindered radical undergoes some copolymerization with ST rather than just β-scission.

The evolution of the MWDs of the NAD systems produced with all three dispersants at the early stages of the polymerization (NAD AS-20, 40 and 60, where the number indicates polymerization time in minutes) are shown in Figure 5.4. The polymer produced during this stage of the reaction remains at lower MW, with the higher MW mode seen in Figure 5.3 not yet formed. The distributions gradually shift to higher MWs as the polymerization proceeds during the particle nucleation stage. A comparison of the MWDs for Dispersant II and NAD AS II-60 in Figure 5.4a shows that there is a greater portion of the higher M_w dispersant chains incorporated into p(MA/ST) copolymer core, compared to the cases shown in Figure 5.4b-c with the utilization of macromer dispersant. This observation is consistent with the interpretations described in the previous chapter: due to the uneven distribution of grafted vinyl groups in Dispersant II, the higher MW chains preferentially react with the added monomers compared to the evenly distributed vinyl-terminated groups among the macromer.

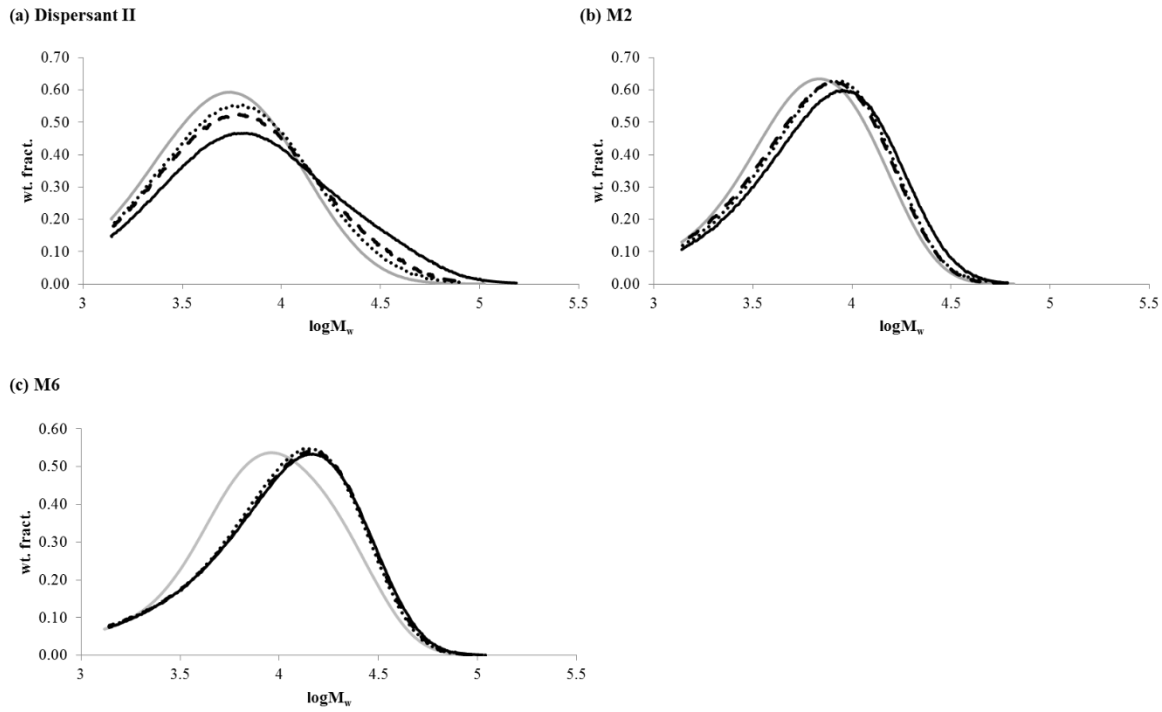

Figure 5.4 MWDs of Dispersants and NAD AS products at the early stage of polymerization: dispersants (grey solid lines), NAD AS-20 (black dotted lines), NAD AS-40 (black dashed lines) and NAD AS-60 (black solid lines). Here the suffix, 20, 40 and 60 indicates the time (min) after the start of the NAD polymerization. (a) Dispersant II; (b) M2 and (c) M6.

The influence of different core compositions on the incorporated amount of dispersant (w_{inc}) is shown in Figure 5.5; for this discussion all results, including NADs with cross-linked cores, are considered. The fraction of dispersant incorporated is lowered when ST is added to the recipes. This is seen by comparing the AS vs A, and the AHSX vs AHX recipes: in all cases and for all three dispersants, decreased values are observed. The cause of this decrease is not obvious: as discussed previously, the addition of ST also leads to a decreased polymer MW. Apart from this, the presence of ST decreases the polarity of the core polymer. As will be discussed in the followed chapter, the nucleation of the particles and reaction partition in the particle phase must

be related to the differences in polarity between the core polymer system and that of the solvent system. Introducing the cross-linking agent (GMA and MAA) and HEA has a smaller effect on dispersant incorporation, as seen by comparing the AX and AHX results to A. The w_{inc} value increases for the grafted dispersant, while almost no change is seen for the macromer dispersants.

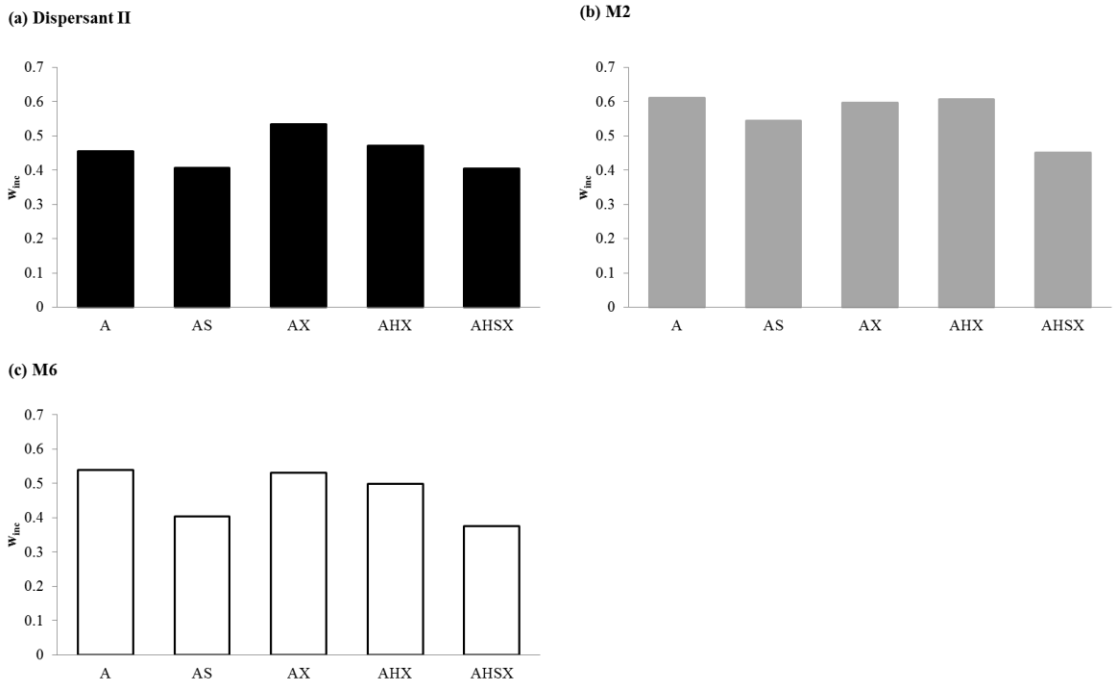

Figure 5.5 The weight fraction of incorporated dispersant measured for NADs made with different dispersants and core compositions: (a) NADs made with Dispersant II; (b) NADs made with M2; (c) NADs made with M6.

The general influence of dispersant choice on the incorporated fraction can be interpreted as discussed in Chapter 4. M2 is more effective than Dispersant II (both with similar M_n values) due to the controlled uniform distribution of the vinyl groups among the polymer chains. It is also

more effective than M6, as a higher vinyl concentration results from the same added mass of macromer to the NAD systems.

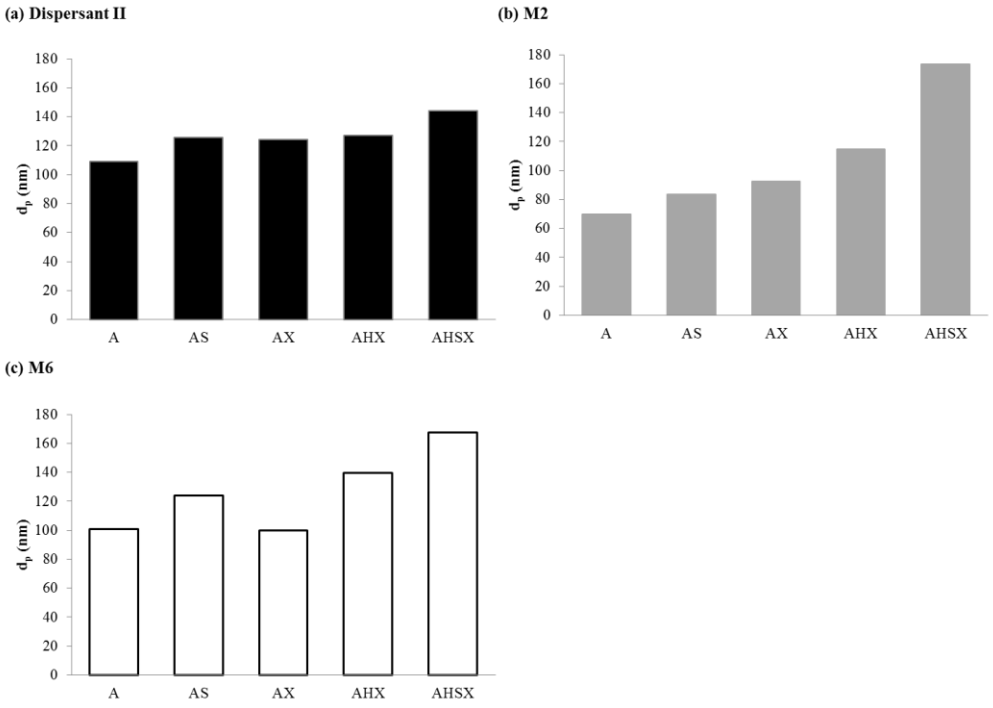

Figure 5.6 Average particle size of NADs made with different dispersants and core compositions: (a) NADs made with Dispersant II, (b) NADs made with M2, and (c) NADs made with M6.

Figure 5.6 shows that the average particle size (d_p) for all NAD compositions produced using the three dispersants is less than 180 nm. However, the variation in size with core compositions is much larger for the macromer dispersants (Figure 5.6b-c) than seen for the standard grafted dispersant (Figure 5.6a). The lower sensitivity of particle size to core composition seen for the grafted dispersant may be due to the fact that only copolymerization (no β-scission) occurs.

The influence of adding a second monomer to the core is also noticed by other researchers.

As reported by Jiang and coworkers,[6] in an MMA/BA copolymer system stabilized by PVP in methanol/water, smaller particles were formed with an increased portion of BA in the core; however, the opposite correlation between d_p and BA amount was noticed for ST/BA copolymer system in ethanol/water utilizing the same stabilizer.[7] Another study reported that particle size increased from 58 to 86 nm with the addition of 1 mol% cross-linker (ethylene glycol dimethacrylate) to hydroxypropyl methacrylate (HPMA) stabilized by block polymer (poly(glycerol methacrylate)-b-pHPMA) through RAFT dispersion polymerization in the aqueous phase.[8] It should be noted that these system depend either on physical adsorption or grafting of the stabilizer to the core polymer through a H-atom abstraction mechanism,[9] in contrast to the covalent bonding between the insoluble polymer and the dispersant that is dominant in our system.

Swelling effect of the uncross-linked NAD particles may affect the measurement of particle size to a greater extent than for the measurements of the cross-linked NADs, as the analysis was done in a heptane/xylene mixture; the related study between the size and the solvent composition is presented in Section 3.3.2. While the extent of this effect might depend on core compositions, it would not explain the differences seen between standard and macromer dispersants. For all three dispersants, there is a consistent increase in particle size between acrylate-only core and AS, and a corresponding particle rise seen between recipes AHX and AHSX. This correlates with the corresponding decreased values of w_{inc} shown in Figure 5.5. This correlations also holds for the cross-linked AX core; as shown in Figure 5.7, an inverse relation is seen between d_p and w_{inc}.

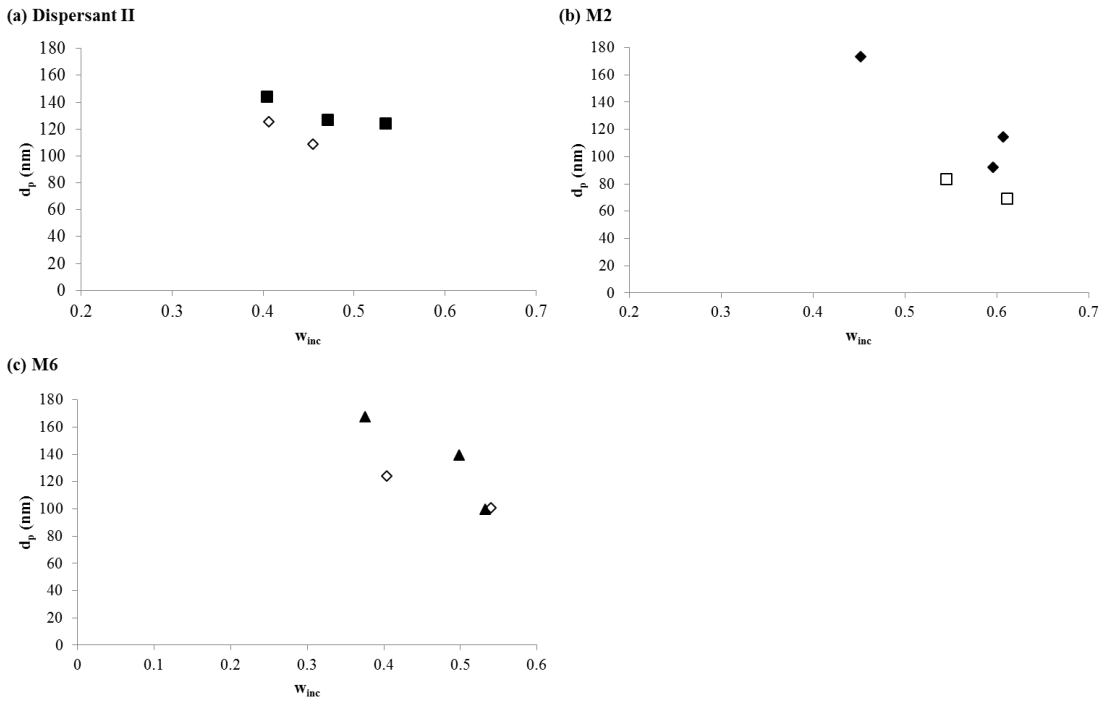

Figure 5.7 The correlation between the average particle size and the incorporated amount of dispersant for uncross-linked NADs (open symbols) and cross-linked NADs (closed symbols): (a) NADs made with Dispersant II, (b) NADs made with M2, and (c) NADs made with M6.

The viscosity of non-aqueous dispersions designed for the coating systems is reported to be 440 cP with 60 wt% solids content,[1] with lower viscosity (< 50 cP) reported elsewhere for NAD systems with ~50 wt% solids.[10] For the systems studied in this investigation, viscosity generally remains below 500 cP with a few notable exceptions, as shown in Figure 5.8. At this point it is difficult to hypothesize the dominant variable that affects the viscosity, as it can be affected by particle size and size distribution as well as the overall solids loading.[11] However, viscosity of NADs made with M6 shows the most variation (160-1500 cP) with the changes in core composition, while viscosity remains low (< 380 cP) for all NADs prepared with M2, another advantage of the lower MW macromer.

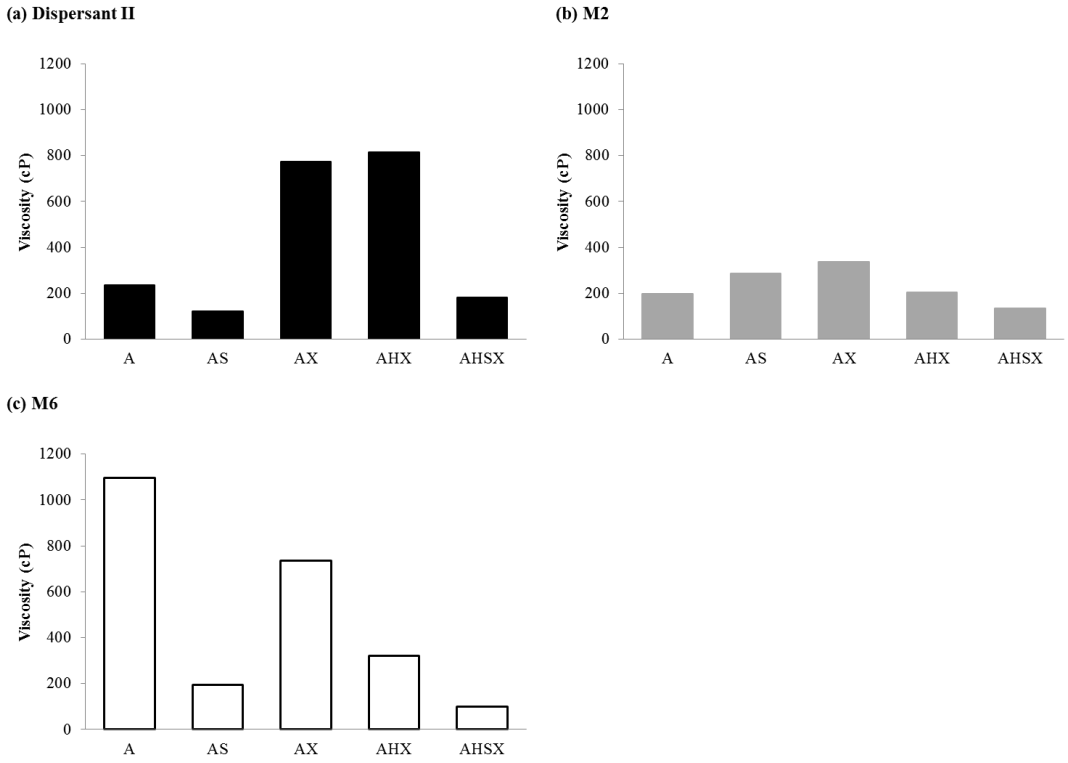

Figure 5.8 Viscosity of NADs made with different dispersants and core compositions: (a) NADs made with Dispersant II, (b) NADs made with M2, and (c) NADs made with M6.

5.3.2 Introducing Higher HEA Content to the Core

Functional hydroxyl groups, either in the particle phase or in the medium, are important for the post-polymerization curing process.[1] Monomers with hydroxyl groups (like HEA) increase the polarity of the core, which benefits the stabilization of the polymer after the non-polar volatile solvents (heptane for example) are evaporated during the spraying atomization. In the previous section, HEA was added to the core mix for a cross-linked system. Here we introduce HEA to an MA/ST copolymer core and gradually increase its fraction from 10 to 20 wt%, a value close to what is shown in the patent (24 wt%).[1] As listed in Table 5.3, the total mass of the monomer mixture (MA/ST/HEA) is kept the same as for the MA homopolymer recipe, with the presence of 10 wt% ST and the utilization of M2 (as the dispersant) constant for the set of experiments.

Table 5.3 Analytical results of NADs prepared with M2 and increased amount of HEA.

Sample	M_n (Da)	M_w (Da)	w_{inc}	d_p (nm)	PdI[a)]	η (cP)
AS	15000	53400	0.55	84	0.25	287
AH10S	16600	61400	0.50	113	0.10	107
AH15S	16600	69000	0.53	130	0.04	68
AH20S	14300	74400	0.71	133	0.05	64

a) Polydispersity of particles by DLS.

The analytical results for this series of NAD reactions are summarized in Table 5.3. M_w increases as more HEA is added to the NAD formula. This may be explained by the kinetics of dispersion polymerization that occurs both in the particle phase and in the continuous phase, with higher M_w polymer normally produced in the particle phase.[12] When pMMA was polymerized in methanol/water mixture at 60 °C using a PVP stabilizer, it was found that M_w almost doubled but M_n only increased by 20% as the conversion increased from 5% to 98% during the batch reaction, a consequence due to the gel effect in the monomer-swollen particle phase and the absorption of low chain length oligomers from the continuous phase into the particles.[13] In the presence of HEA earlier nucleation of particles is seen (Appendix A.3.1), as it is a more polar ingredient than MA and ST. Thus, less affinity between the core copolymer (MA/ST/HEA) and aliphatic solvent (heptane/xylenes) can be assumed, leading to growing radicals with shorter critical chain lengths and earlier precipitation from solution. As the polymerization proceeds, there might be a greater portion of reaction undergoing in the particle phase, where higher overall M_w is expected, rather than in the continuous phase; a kinetic study of MMA in cyclohexane (dispersion polymerization) and benzene (solution polymerization) found that pMMA with higher M_n is produced via dispersion polymerization.[12] In addition, the faster propagation rate of HEA compared to other acrylates may also lead to an increase in the final M_w.[14]

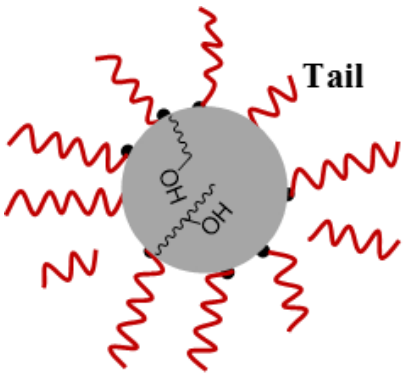

Figure 5.9 Schematic of the possible location of the hydroxyl groups belonged to HEA in the particles stabilized by macromer dispersant.

Table 5.3 also shows that there is little effect of HEA amount (10 and 15 wt%) on the incorporated fraction of dispersant, although a larger increase is observed for AH20S (20 wt% HEA). The opposing influence of ST and HEA may balance out for the system; as previously observed (Figure 5.5), ST weakens and HEA improves the utilization of dispersant. A clear increase in average particle size as well as a narrowed size distribution is observed with the increased amount of HEA in the system. This may be a result of the lowered affinity between the core and the medium in the presence of the more polar HEA content. Note that the addition of HEA to the cross-linked system also leads to an increase in particle size for the macromer dispersants (see Figure 5.6). The viscosity of the system significantly decreases with the HEA content, despite the addition of -OH groups that are known to increase solution viscosity through hydrogen bonding. It is reasonable to hypothesize that there is a very high fraction of the HEA moiety "buried" inside of the core due to its high polarity, rather than close to the particle surface, as depicted in Figure 5.9. Thus, the H-bonding caused by the addition of HEA to the system is contained within the particles, not influencing the overall NAD viscosity.

5.3.3 The Investigation of New Feeding Strategy and Reduced Amount of Dispersant

A study on the impact of dispersant feeding strategy, as well as reduced amount of dispersant and increased core content, has been conducted with the grafted dispersant, as described in Section 3.5. Slightly higher M_w and a minor increase in particle size were seen when all dispersant was added initially. Reducing the amount of dispersant led to larger particles and higher M_w, with the same results observed for an increased monomer amount in the core. The similar experimental practices were also conducted to examine the properties of the NADs prepared with macromer dispersant.

The reproducibility of NADs made with M2 (new batch of macromer provided by Axalta Coating Systems) is shown in Appendix Table A.3.1, with similar properties obtained compared to the previous results. The standard feeding method (adopted from the patent literature[1]) of the dispersant solution is to add 2/3 of the total quantity initially, with the remainder fed with the monomer loading. The believed justification for this strategy is that it is necessary to add dispersant throughout the reaction to ensure that dispersant chains containing double bonds are available throughout the entire semibatch reaction. With macromer as dispersant, however, it is known that every dispersant chain contains a reactive double bond. In this set of experiments, one-step loading method (all dispersant added initially) was investigated as a potential simplification of the current process, using both MA homopolymer and MMA/MA copolymer cores. The lower molecular weight macromer, M2, was utilized for the study.

Results for the experiments conducted with an MA homopolymer core, including an investigation of reducing the amount of dispersant, are summarized in Table 5.4. First, let us compare the two different feeding methods (Standard vs New): the MW averages of the two products are similar, with a slight increase in M_w (98600 vs 91500 Da) observed when all dispersant is added at the start of the reaction, similar to the result observed for NAD made with grafted dispersant. However, viscosity increases from 500 cP (Standard) to 1000 cP (New), which

may be due to the slight decrease of average particle size from 73 (Standard) to 68 nm (New). The incorporated amount of dispersant increases quite significantly, from 0.62 to 0.84, with the new feeding method. This observation, along with the smaller particle size, may result from the higher concentration of reactive macromer present from the start of the batch. A larger fraction of dispersant is utilized, as the total surface area of particles increases with the decreased particle size under the same monomer loading.[15]

Table 5.4 Analytical results of MA homopolymer NADs made with M2, and with different feeding strategies, reduced amount of macromer and added extra MA.

Sample	M_n (Da)	M_w (Da)	w_{inc}	d_p(nm)	PdI	η (cP)	Expected solids
Standard	16500	91500	0.62	73	0.05	490	0.552
New	17200	98600	0.84	68	0.06	958	0.552
New-75%	17500	96400	0.73	75	0.09	684	0.546
New-50%	18200	93400	0.65	86	0.07	388	0.539
New-75%+10	18100	97900	0.75	74	0.07	1928	0.563
New-75%+15	18400	103400	0.86	79	0.10	-	0.570

Based on this encouraging finding, reduction of the total amount of dispersant added to the system was investigated. As shown in Table 5.4, it is feasible to reduce the amount of dispersant in the system up to 50% with the new feeding method, as stable MA homopolymer NAD was still obtained. Particle size increases slightly with the reduced dispersant amount. Polymer MWs are not greatly affected, and the value of w_{inc} decreases back to 0.65 as dispersant concentration is reduced. Viscosity of the NAD solution is also greatly reduced, perhaps as a result of the larger particles formed. A comparison between the properties of NADs prepared with

less dispersant and different stabilizers (macromer and grafted dispersants) is summarized and discussed at the end of the section.

The overall solids content in the NAD system decreases when less dispersant is used. Thus it offers the opportunity to increase the amount of monomer to form the particles. Table 5.4 summarizes the results obtained when the MA monomer used in the core recipe is increased by 10 and 15 wt% (New-75%+10 and New-75%+15), with the dispersant amount kept at a level of 75% of the original amount with the new feeding strategy. MW increases slightly with higher monomer loading, a result of the higher ratio between monomer concentration and initiator concentration. The incorporated amount of dispersant remains high and average particle size is small. However, viscosity surges and the value of New-75%+15 is out of the instrument's measurable limit (>2000 cP). Thus, there is a limit to increasing particle content in this recipe. Another literature study reaches the same conclusion, as a broadened particle size distribution and even coagulum were observed when monomer content was increased from 38 to 63% for the production of ST homopolymer particles stabilized by PVP in ethanol.[16]

As part of the core composition study, it is also of interest to investigate the effect of feeding method and dispersant amount on the MMA/MA copolymer recipe produced with M2. The same set of experiments was repeated, using the new feeding method with reduced dispersant and extra monomer. Table 5.5 shows that similar M_w values are obtained for B-M2 (standard feeding method) and F100B-M2 (new feeding method). Better dispersant incorporation and smaller particle size are seen for F100B-M2, as compared with B-M2. Viscosity slightly increases from 154 to 163 cP when the new feeding method is applied to prepare NAD.

For the copolymer system, it is possible to reduce the amount of dispersant only by 25%, as a further decrease resulted in coagulation of particles. As a result of the chain transfer mechanism that occurs in the presence of methacrylate, there is an increased chance that the macromer is not chemically attached to the core. This makes the BMA macromer less effective in

the base formula than that in the MA homopolymer recipe. M_w of F75B-M2 increases as compared to B-M2, which may be due to the reduced transfer reaction between macromer and MMA in the condition of less dispersant. Larger particles and lower viscosity are obtained, the same trends seen for the MA only systems.

The amount of monomer added to the core recipe with the reduced dispersant was increased by 10 wt%, the experiment labeled as F75B10-M2 in Table 5.5. The increased core monomer loading led to a further increase in MW, d_p and viscosity, with no change observed for w_{inc}. These conclusions are close to what has found for NADs made with the MA core under the same conditions. However, variations on the reaction conditions seem to have a bigger impact on MW and d_p and less effect on viscosity for copolymer systems, a result likely due to the formation of larger particles (>100 nm).

Table 5.5 Analytical results of MMA/MA copolymer NADs made with M2, and with different feeding strategies, reduced amount of macromer and extra core monomer.

Sample	M_n (Da)	M_w (Da)	w_{inc}	d_p(nm)	PdI	η (cP)
B-M2	12200	42900	0.41	104	0.22	154
F100B-M2	12100	41500	0.61	97	0.23	163
F75B-M2	14900	62200	0.66	124	0.17	55
F75B10-M2	15800	72700	0.66	135	0.17	83

Table 5.6 summaries the effect of reduced dispersant on NAD properties when M2 and Dispersant II (results from Chapter 3) were utilized. When there is less dispersant present in the system, larger particles and less viscous dispersion systems are normally seen, regardless of the type of dispersant and the core composition employed. However, the opposite results of w_{inc} and M_w for NADs with MA and MMA/MA core compositions are seen when M2 is utilized. The

reason might be the different polymerization mechanism of the methacrylate-type macromer with MMA and MA, as it copolymerizes with MA while undergoes chain transfer reaction with MMA.

Table 5.6 The effect of reduced amount of dispersant on NADs made with M2 and Dispersant II, and with MA and MMA/MA core.

	NADs made with M2[a)]		NADs made with Dispersant II[b)]
	MA	MMA/MA	MMA/MA
d_p (nm)	↑	↑	↑
M_w (Da)	↓	↑	↑
w_{inc}	↓	↑	—
η (cP)	↓	↓	—

a) NADs prepared via the new feeding method.
b) NADs prepared via the standard feeding method.

5.4 Conclusions

A series of NADs were made with different core compositions with both the standard grafted dispersant, as well as the new macromer dispersants. These products were all stable, with high solids content (60 wt%), small particle size (< 180 nm) and low viscosity (< 1000 cP), features desired for potential commercial application. NADs made with MA homopolymer core, regardless of the utilized dispersants (grafted and macromer dispersants), have the smallest d_p and highest fraction of incorporated dispersant. Introducing cross-linker (5.8 wt%) and HEA (10 wt%) to the core results in larger d_p and slightly higher fraction of incorporated dispersant.

However, the addition of 10 wt% ST had a much larger impact compared with the other three ingredients, which may be due to the formation of sterically hindered radical during reaction with macromere, and the slower polymerization rate of ST. In general, particle size showed a greater sensitivity to the core composition with macromer dispersant compared to the standard grafted dispersant. This result needs to be further explored to support the use of the more efficient macromer dispersants under industrial conditions.

Increasing the fraction of HEA amount to MA/ST core from 10 to 20 wt% leads to a good incorporation of the macromer dispersant, small particles and low viscosity, suggesting that the system will be robust at high content of functional hydroxyl groups in the core recipe. All dispersant added initially improves the efficacy of the macromer dispersant and slightly decreases particle size in the dispersions, with a greater increase seen for the viscosity. When less dispersant is added to the MA and MMA/MA core, the main features of NAD are maintained. It is also possible to match the loss of the solids content (due to the reduced dispersant used) with added core material, as higher MW, average particle size and viscosity are seen. However, viscosity seems to increase rapidly when this strategy is applied to the MA-homopolymer recipe. Further investigation of this result, which may be somewhat related to the small particles formed for this system, is required.

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Chapter 6

Investigation of Macromer Dispersants with Hydroxyl Groups

6.1 Introduction

Hydroxyl alkyl acrylates and methacrylates are important ingredients in NAD products, since the functional group speeds up the curing process in the production line[1] and improves damage resistance through cross-linking for the coatings.[2] As primary alcohols, HEA and HEMA allow faster baking speed for top coat applications, and HEMA also enhances UV durability.[3] In the last chapter, the influence of adding HEA to the core recipe was investigated. This chapter looks at the influence of adding HEMA to the methacrylate macromer dispersant. BMA/HEMA macromer has been employed as a dispersant to study the effect of hydroxyl groups on NAD synthesis. Various feeding strategies are explored and the influence of core compositions on NAD properties is investigated. In addition, Hansen solubility parameters are introduced as a means to understand the effect of the core and dispersant composition on the polymer solubility and NAD stability.

6.2 Experimental

The reactor, monomers, initiator, solvents, and operating procedures were the same as previously described in Chapter 5, with any differences stated in the discussions. Macromer dispersants with three different levels of hydroxyl groups were kindly provided by Axalta Coating Systems as 60 wt% solution in xylenes and similar M_n to BMA macromer (M5, see Chapter 4). As summarized in Table 6.1, the macromers with higher HEMA content has slightly lower MW values. The influence of core compositions was investigated using BH5, with 10 wt%

ST, 10 wt% HEA and 5.8 wt% cross-linker (1.6 wt% GMA and 4.2 wt% MAA) gradually introduced to the MA and MMA/MA cores.

Table 6.1 Macromer dispersants utilized for the preparation of NADs.

Sample	composition (BMA/HEMA)	M_n (Da)[a)]	M_w (Da)[a)]
M5	100/0	7100	12000
BH5	95/5	7800	14200
BH10	90/10	6500	11800
BH15	85/15	5400	9200

a) MW values are reported according to polystyrene calibration (used as the standards for SEC analysis), without further correction.

Measurements of molecular weight, average particle size and viscosity were conducted via size exclusive chromatography (SEC), proton nuclear magnetic resonance (^{1}H NMR), Malvern Zeta-Sizer Nano ZS, and the Brookfield Viscometer, respectively, as described in Section 4.2.5. However, the quantification of dispersant incorporated with the core differed due to the presence of the hydroxyl groups in the macromer. While heptane was used as the extracting solvent in the previous chapters, a heptane/xylenes mixture (H8X2, 8/2, w/w) was also utilized to extract the soluble polymer remaining in the medium for NAD products using BH5, with the same centrifugation procedure (at 6000 rpm for 10 min).

6.3 Results and Discussions

In the previous chapter, the introduction of 10-20 wt% HEA into the MA/ST core was shown to have only a minor influence on the dispersion polymerization, with the features of NAD products maintained (low viscosity and small particle size). As a result of this encouraging

finding, macromer dispersants prepared with different levels of HEMA units were subsequently investigated to study their effects on NAD systems, as the ability to cross-link free dispersant in the dispersion into the final coat is also desired for the post-polymerization application. Previous studies have demonstrated that it is promising to simplify the dispersant feeding method to the new feeding strategy (all dispersant added initially); thus, this methodology was applied in most cases investigated in this chapter.

6.3.1 NADs Synthesized with Higher HEMA Segment in BMA/HEMA Macromers

BMA/HEMA macromers with higher HEMA levels (10 and 15% in the copolymer composition, labelled as BH10 and BH15) were first investigated as dispersants for NADs with MA homopolymer core, using both the standard and the new feeding methods. It was found that NADs synthesized with these macromers were unstable, as sedimentation of the particles was observed after the reaction, regardless of the dispersant feeding methods. Figure 6.1 shows a comparison between a stable NAD product (NAD A-BH5, discussed in the followed section) and an unstable one (NAD A-BH10, produced with MA homopolymer core and BH10 dispersant), for which two separated phases are observed. The poor performance of BH10 and BH15 is surprising, but likely results from the increased polarity of the macromer with HEMA present: the more polar macromers may favor the more polar particle phase over the less polar continuous phase, such that a higher fraction of the BMA/HEMA macromer becomes buried inside of the particles, not extending into the medium or attaching on the particle surface.

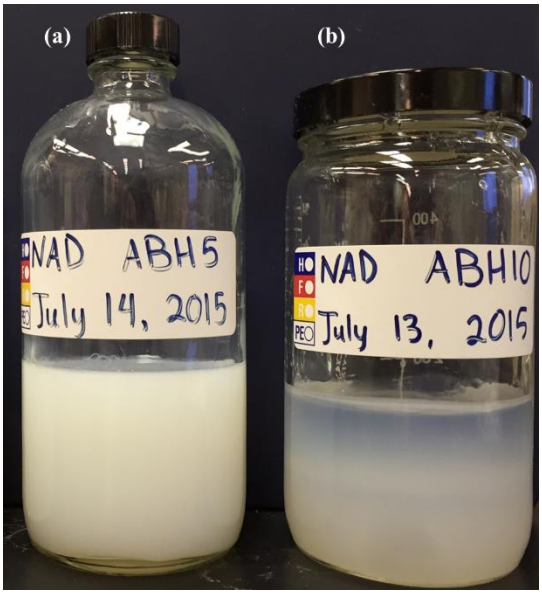

Figure 6.1 Photographs of NAD products prepared with MA homopolymer and BMA/HEMA macromers: (a) stable NAD A-BH5; (b) unstable NAD A-BH10.

6.3.2 The Comparison between BMA Homopolymer Macromer and the BMA/HEMA Copolymer Macromer

Although unstable NADs were prepared with BH10 and BH15 (higher HEMA content), it was feasible to produce stable NADs with the BH5 macromer, containing 5% HEMA. Table 6.2 summarizes the analytical results for the NAD BH5 products compared to those produced with M5, the BMA macromer containing a similar chain length: "A" is MA homopolymer core with standard feeding; "FA" is MA homopolymer core with the new feeding method; "FAX" is cross-linked MA core with the new feeding method.

The M_w of NAD A-BH5 is slightly lower than that of A-M5, an unexpected result, as the BH5 dispersant has a higher M_w than M5 (see Table 6.1). This may be due to the higher polarity of the HEMA units contained in the dispersant. In addition, the BH5 dispersant solution is more viscous (by visual observation) than M5 solution with the same MW and solids content, another

factor that may influence the MW of final NAD product. MWDs of samples taken at the beginning of polymerization for NAD A-M5 and NAD A-BH5 are illustrated in Figure 6.2, with similar distributions for NAD A-20, 40 and 60 (samples at 20, 40 and 60 min) seen in both cases; a higher M_w portion is seen for NAD A-M5-120 compared with NAD A-BH5-120, an indication of the higher M_w obtained for the NAD A-M5 final product.

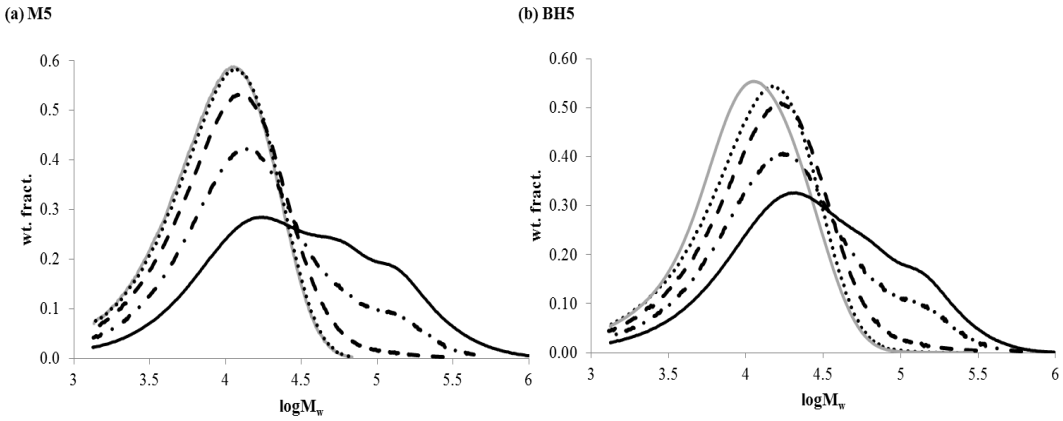

Figure 6.2 MWDs of Dispersants and NAD A products at the early stage of polymerization: dispersants (grey solid lines), NAD A-20 (black dotted lines), NAD A-40 (black dashed lines) and NAD A-60 (black dashed-dotted lines) and NAD A-120 (black solid lines). Here the suffix, 20, 40, 60 and 120, indicates the time (min) after the start of the NAD polymerization. (a)M5; (b) BH5.

Table 6.2 Analytical results of NADs prepared with M5, BH5 and different feeding methods.

Sample	M_n (Da)	M_w (Da)	w_{inc}	d_p (nm)	PdI	η (cP)
NAD A-M5[a)]	16200	71100	0.56	83	0.08	874
NAD FAX-M5	-	-	0.79	89	0.10	1570
NAD A-BH5	15800	61200	0.95	92	0.08	high
NAD FA-BH5	17100	69400	0.94	90	0.08	high
NAD FAX-BH5	-	-	0.97	93	0.11	high

a) The same NAD sample studied in Chapter 4.

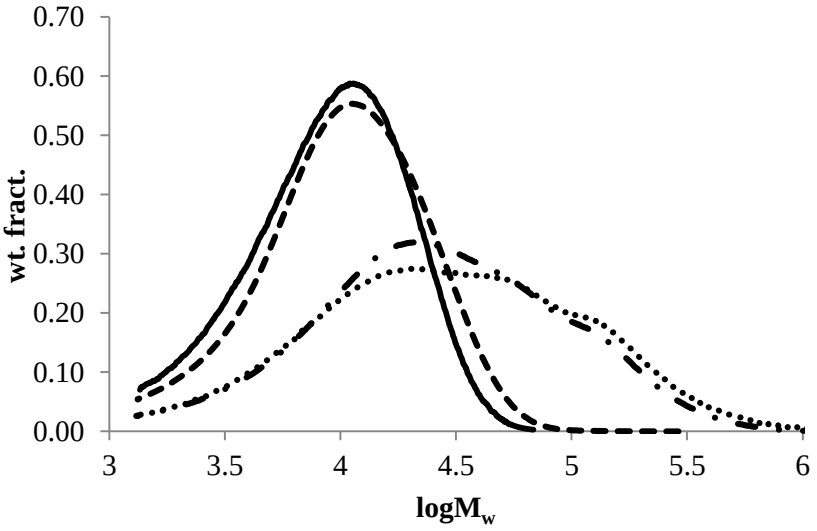

Figure 6.3 MWDs of macromer dispersants and NADs: M5 (solid line), BH5 (dashed line), NAD A-M5 (dotted line) and NAD A-BH5 (dashed-dotted line).

When the BMA-type macromer dispersant is replaced with the BMA/HEMA copolymer, there are two major differences seen in the analysis of the final NAD product. Firstly, the viscosity of the NAD is found to be much higher. This can be understood by the presence of H-

bonding from the dispersant, which will increase the interactions between particles and BH5 chains remaining in the solution and adsorbing on the particle surface. Secondly, a significant increase in the fraction of incorporated dispersant (>0.9) is noticed for NAD A-BH5 compared to the values of 0.5-0.6 found for NAD A-M5. While this might indicate increased effectiveness of the dispersant, the measured MWDs show the opposite: as plotted in Figure 6.3, a significant fraction of lower M_w material is still found in the product (comparable to that found with M5 dispersant), indicating that, while the HEMA containing macromer was not in solution (at least when isolated using the heptane procedure), it also had not reacted with the MA core chains.

The MWDs of the macromer dispersants and the soluble polymers recovered from the extraction by heptane are shown in Figure 6.4. MWDs of the BMA macromer and the corresponding soluble polymer recovered from NAD are almost identical, a result shown before (see Chapter 4) and attributed to the even distribution of vinyl group among the BMA macromer chains. The behavior with the HEMA containing macromer is different, as Figure 6.4b shows that the soluble polymer recovered from NAD A-BH5 is of lower MW than that of the original macromer. Two explanations can be proposed to explain this observation. The desired role of macromer is to react with the core chains, and stabilize on the colloidal surface. However, it may also physically adsorb to the surface, or become absorbed (or react) into the interior of the particles. It is reasonable to hypothesize that there are more HEMA units in the longer chain length BH5 macromer, such that these chains prefer to adsorb/absorb into the particles rather than extend in the continuous phase. In addition, the higher polarity of BH5 (as compared to BMA macromer) may lead to its overall poorer solubility in the heptane added to separate the particles from the continuous phase, such that it remains with the more polar core phase. Thus, only the polymer with shorter chain length (and perhaps reduced HEMA content) is recovered from the dispersion. To investigate this possibility, other solvents (more polar solvents) were tested to

extract the soluble polymer in the NADs produced with BH5, as discussed in the followed section.

The high viscosity of NAD A-BH5 may also be an indicator of the presence of free dispersant, as stronger intermolecular force is expected from the –OH groups on the HEMA moiety. Larger particles are obtained for NAD A-BH5, as compared with NAD A-M5, a result that may be due to slightly less concentrated vinyl groups (higher M_n of BH5); but it is likely an indication of the decreased effectiveness of the HEMA-containing macromers since the usage of BH10 and BH15 results in unstable NADs.

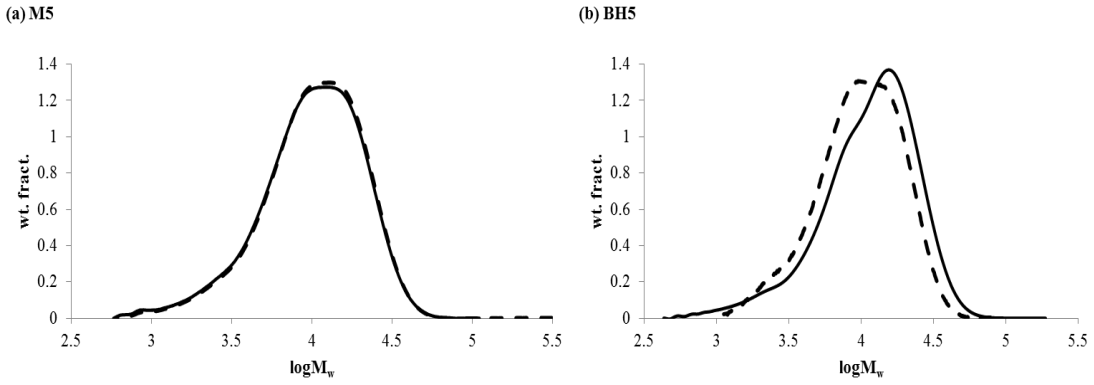

Figure 6.4 MWDs of dispersants (solid lines) and soluble polymers recovered from NADs by heptane treatment (dashed lines): (a) M5 and NAD A-M5; (b) BH5 and NAD A-BH5.

Table 6.2 also shows that the feeding strategy has little effect on these findings, with slightly higher M_w and smaller d_p produced for NAD FA-BH5; the same minor impact was seen for the NADs prepared with BMA-type macromers, as reported in Chapter 5. Larger particles are produced (NAD FAX-M5 and FAX-BH5) in the presence of cross-linker, a result consistent with the findings reported in the previous chapter.

6.3.3 NADs Prepared with MA Dominated Core

The influence of core composition on the performance of the HEMA-containing macromer remains of interest, as the physical and chemical properties can be introduced to improve the performance of the NAD system. As studied in the previous chapter, the NAD particle size increased with additional monomers added to the MA homopolymer system. The same methodology (10 wt% ST and 10 wt% HEA) was applied for this set of experiments with BH5 macromer and all dispersant added at the start of the reaction.

As summarized in Table 6.3, the fraction of incorporated dispersant (w_{inc_H8X2}) determined by applying the heptane/xylenes mixture (8/2, w/w) for NAD FASX and FASHX is similar to that of homopolymer MA NADs prepared with BMA macromer. This is in contrast with the high values of $w_{inc\_heptane}$ which, as discussed previously, does not provide an accurate evaluation of the fraction of dispersant incorporated with the core polymer chains. MWDs of soluble polymer recovered from the two sets of experiments are plotted in Figure 6.5a and 6.5b, with the distributions of soluble polymer extracted by heptane for comparison. While there might be a fraction of higher M_w polymer dissolved in the H8X2 mixture, as xylenes are better solvent, it is seen that the MWDs of the soluble polymer fraction are quite similar to that of the original BH5 macromer, compared to the soluble polymer isolated by using pure heptane. A further study looking at the extraction by pure xylenes for a NAD sample produced with 10 wt% cross-linker and an MA based core shows that the soluble polymer recovered has even higher M_w compared to the original dispersant (see Appendix A.4.1), suggesting that low MW core chains are being extracted from the particles during the analytical procedure. Neither extraction procedure is perfect: adding pure heptane as the extracting solvent may cause free BH5 dispersant to precipitate/adsorb onto particles, while the heptane/xylenes mixture may extract some of the physical adsorbed dispersant from the particles. In both cases, the shift in MWDs relative to the original dispersant is most likely due to the polarity difference of the dispersant via extraction. Of

these two cases, however, the mixed solvent provides a better estimate of w_{inc}, as the MWD of the recovered soluble polymer better matches with that of the original dispersant, as the similar distributions of the dispersant and the recovered polymer would be expected due to the uniform distribution of double bonds in the macromer chains.

Table 6.3 also shows that larger particles are formed when ST is in the core for NAD FASX, as compared to NAD FA and FAX, the same result observed for NAD formulations prepared with M2 (see Chapter 5). The largest particles are produced with NAD FASHX, which may be due to the polar HEA content, as the oligomers (short chain length polymer produced during the polymerization) and BH5 with HEMA moiety may prefer to interact with the particle phase rather than within the non-polar heptane/xylenes medium. However, the average particle size remains less than 150 nm, and viscosity drops significantly with the increased particle size, showing a promising application of NADs made with the low HEMA content BMA/HEMA macromer.

Table 6.3 Analytical results of NADs prepared with BH5, MA dominated core and the new feeding method.

Sample	$w_{inc\_heptane}$ [a)]	w_{inc_H8X2} [b)]	d_p (nm)	PdI	η (cP)
FASX	0.95	0.52	135	0.10	287
FASHX	0.89	0.74	149	0.04	241

a) Heptane was used as the extracting solvent.

b) H8X2 was the extracting solvent.

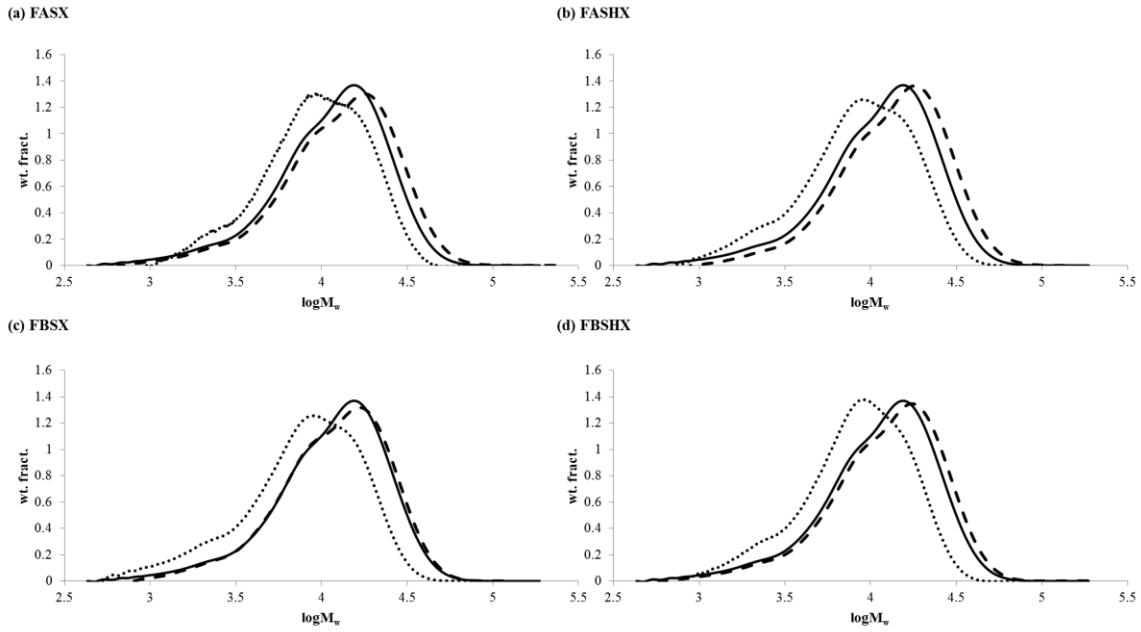

Figure 6.5 MWDs of BH5 and soluble polymers recovered from NADs prepared with BH5 and different core compositions: BH5 (solid line), soluble polymer extracted by heptane (dotted lines), and soluble polymer extracted by H8X2 (dashed line). (a) NAD FASX, (b) NAD FASHX, (c) NAD FBSX, and (d) FBSHX.

6.3.4 NADs Prepared with MMA/MA Dominated Core

As stated in the previous chapter, MMA is an important ingredient for high T_g coating products. Thus, the base copolymer case (MMA/MA) was also investigated utilizing the BMA/HEMA macromer with the new feeding strategy; the mass ratio between MMA and MA was kept the same as described in Chapter 4. Cross-linker (5.8 wt%), styrene (10 wt%) and HEA (10 wt%) were then introduced to the core, as done for the acrylate-based NAD systems.

Table 6.4 Analytical results of NADs prepared with BH5, MMA/MA dominated core and the new feeding method.

Sample	$w_{inc\_heptane}$ [b]	w_{inc_H8X2} [c]	d_p (nm)	PdI	η (cP)
B-M5 [a]	0.36	-	135	0.17	117
FB	0.97	-	154	0.21	263
FBX	0.97	0.52	378	0.16	high
FBSX	0.96	0.83	251	0.16	229
FBSHX	0.96	0.75	354	0.09	1532

a) The same NAD sample studied in Chapter 4, prepared with M5, MMA/MA copolymer and standard feeding method.

b) Heptane was used as the extracting solvent.

c) H8X2 was the extracting solvent; data for NAD B-M5 and FB-BH5 was not available.

Table 6.4 summaries the analytical results of NADs prepared with MMA/MA dominated core. The incorporated fraction of dispersant calculated with the heptane extraction for the NADs prepared with BH5 is much higher than that of NAD B-M5, a result due to the poorer solubility of BH5 in heptane. As for the MMA/MA copolymer NADs, supporting evidence for this conclusion is provided by an examination of the MWDs of the soluble polymer extracted by heptane for NAD FBSX and FBSHX, which are shifted to lower MWs compared to the original dispersant (Figure 6.5c and 6.5d). The lower w_{inc_H8X2} values are likely more indicative of the actual fraction of BH5 incorporated into the core particles. The values are higher than the value of $w_{inc\_heptane}$ determined for NAD B-M5 but, due to the differences in procedure, it is difficult to conclude whether this is meaningful. Using BH5, an inverse correlation between w_{inc_H8X2} and d_p is observed. Much larger d_p values are obtained with the MMA/MA core compared to acrylate only systems; however, low viscosity is not seen for this set of experiments. It seems that the NAD systems synthesized with the MMA/MA dominated core are more sensitive to recipe changes than MA based core, as also seen for MMA/MA NADs prepared with BMA-type

macromers in Chapter 5. The reason for this sensitivity is unclear, although the chain transfer reaction between the MMA and methacrylate-type macromer may play a role.

6.3.5 Hansen Solubility Parameter of the NAD Systems

In the coatings industry, solubility parameters are often applied to ensure compatibility between solvent and polymer in a homogeneous mixture. In this section, the concept is applied to the heterogeneous NAD system. It is clearly desirable that the core polymer is incompatible with the solvent mixture to promote particle nucleation, while the dispersant should be compatible with the solvent such that after it reacts into the core polymer chains it can remain on the particle surface and extend into the solvent to stabilize the particles. In addition, the solvency of the medium affects the critical chain length of the oligomer produced, a parameter influencing the nucleation of particles.[4] Here, Hansen solubility parameters are used to interpret the experimental results of this thesis, with the goal of understanding the performance of BMA/HEMA macromers in particular.

The thermodynamic equation of the mixing is given by the Gibbs free energy, as shown in Equation 6.1.[5]

$$\Delta G_m = \Delta H_m - T\Delta S_m \tag{6.1}$$

where ΔG_m is the Gibbs free energy; ΔH_m is the enthalpy; ΔS_m is the entropy. In order to get two materials mixed, ΔG_m should be negative. Otherwise, phase separation will occur. Dissolution of a high MW polymer generally results in a change of entropy such that change of enthalpy is crucial. The solubility parameter is defined to describe the mixing enthalpy.[5]

The original solubility parameter is defined by Hildebrand[6] as the square root of cohesive energy density, as presented in Equation 6.2,

$$\delta = \sqrt{\frac{E}{V}} = \sqrt{\frac{\Delta H_{vap} - RT}{V}} \quad (6.2)$$

where E is the energy of vaporization, and ΔH_{vap} is the enthalpy of vaporization. However, use of this parameter is limited for polymer systems, as polymers are already degraded before vaporization.

Hansen[7] proposed a means to expand the concept, with E broken into three intermolecular forces: a dispersive force (non-polar interaction), a polar cohesive force (dipole-dipole interaction) and hydrogen bonding. Thus, the Hansen solubility parameter is similarly composed of three parts, as expressed in Equation 6.3

$$\delta^2 = \delta_d^2 + \delta_p^2 + \delta_h^2 \quad (6.3)$$

where δ_d, δ_p and δ_h are the dispersion force, polar force and hydrogen-bonding effect, respectively.

A qualitative methodology is investigated for the preliminary study of the effect of the solubility difference on the NAD systems. The definition of solubility distance between the polymer and the solvent, R_a, is shown in Equation 6.4. This parameter is then used to evaluate the relative energy difference (RED) number, Equation 6.5, which has been applied in the coatings industry to predict the solubility behavior of the polymer in solvent.[7]

$$R_a = \sqrt{4(\delta_{d,1} - \delta_{d,2})^2 + (\delta_{p,1} - \delta_{p,2})^2 + (\delta_{h,1} - \delta_{h,2})^2} \quad (6.4)$$

where δ_d, δ_p and δ_h are the non-polar dispersion forces, polar forces and hydrogen-bonding effects of polymer (1) and solvent (2), respectively.

$$RED = R_a/R_o \quad (6.5)$$

In Equation 6.5, R_o is an experimentally determined number describing the solubility radius of a polymer. An RED number equal to 0 indicates no energy difference between the solute and the solvent (hence, excellent compatibility), while a RED number less than 1 still shows reasonable

affinity between polymer and solvent. A value close to 1 represents a boundary situation in terms of polymer solubility in the solvent, and higher number suggests poor affinity.

Solubility parameters have been introduced in a few literature studies to interpret dispersion systems with varied monomer[8] and solvent compositions.[9,10] In one effort, dispersion polymerization of five different alkyl methacrylate monomers was investigated in a methanol/water mixture (polar medium) with PVP used as stabilizer; the solubility parameter decreased for the longer alkyl chains (less polar monomers), indicating lower compatibility with the polar solvent mixture.[8] While smaller particles were produced with these less polar monomers, it was found that the average particle size formed by poly(2-ethylhexyl methacrylate) and poly(lauryl methacrylate) was less sensitive to the change of medium polarity (by increasing the methanol amount in the binary solvent), as compared to the sizes synthesized with pBMA, poly(ethyl methacrylate) and pMMA through homopolymerization. The solvency of the reaction medium (relative to that of the polymer being formed) plays an important role in the polymerization, as it affects the critical chain length (j_{crit}) of the polymerizing chains; thus it will influence the particle size in the heterogeneous system.[9] Smeets et al.[4] demonstrated that higher values of j_{crit} were observed for pMMA oligomers with increased temperature, lowered polymer concentration, and higher methanol content in a binary water/methanol mixture. Another study conducted with ST/BMA copolymer stabilized by hydroxypropyl cellulose (HPC) in ethanol/water showed that smaller and narrow distributed particles were formed as the water fraction was increased from 2 to 14 vol%, thus increasing the polarity of the solvent relative to the non-polar copolymer.[9] The influence was greater under the same reaction conditions (stabilizer, solvent mixture and monomer concentration) for copolymers containing a higher fraction of the less polar BMA moiety.[9] Lok and Ober[10] discussed dispersion polymerization of ST with the steric stabilizer HPC in methyl cellosolve (MeCell)/ethanol and illustrated that mono-

dispersed and larger particles were produced with the increased MeCell portion in the solvent mixure (better affinity between the core polymer and the medium).

Table 6.5 Hansen solubility parameters of monomer, pure solvents and homopolymers.

Sample	δ_d [a)]	δ_p [a)]	δ_h [a)]	δ
heptane	15.3	0	0	15.3
p-xylene[b)]	17.8	1	3.1	18.1
MA	15.3	6.7	9.4	19.2
pMA	17.4	4.3	6.5	19.1
pBMA	16.1	1.4	3.5	16.5

a) Data from HSPiP software and units are $MPa^{1/2}$.
b) p-xylene represents the mixed xylenes which is used as the solvent for the dispersant solution.

The aforementioned research studies were done in batch reactions, in which the presence of the monomer at the start of the reaction influences the polarity of the continuous phase. A limited number of batch reactions were conducted during this thesis in a supervised 4th year undergraduate project, to explore whether the simplified experimental process may help with the interpretation of particle nucleation in our NAD system. The batch experiments were kept to 40 wt% solids content, as further increasing the solids led to a very viscous system. The experimental procedure is described as followed: 43.5 g M2 solution (BMA-type macromer, described in Chapter 4), 116.2 g heptane and 61.7 g MA were added to the Labmax reactor and heated up to 92 °C; an initiator shot of 1.3 g butyl acetate and 0.55 g Vazo® 67 was added before polymerization started; then a mixture of 3 g butyl acetate and 0.55 g Vazo® 67 was dosed to the reactor within 30 min; the reaction mixture was held for 45 min before it cooled down to room temperature. Variations of experimental conditions regarding of the dispersant amount are summarized in Table 6.6, and Table 6.5 lists Hansen solubility parameters (δ, HSPs) of MA and

pure solvents estimated through HSPiP 5.0.03 software, the same computer program applied to predict the partition behavior of cytotoxic solutes between polymer phase and aqueous phase.[11]

Calculation of the solubility parameter of the initial dispersion systems is via the root-mean-square weight average of δ of the solvents and the monomer without the input from the stabilizer and the polymer produced, as the reactions were performed in batch. The correlation between the average particle size and HSPs of the initial system (δ_{system}) is summarized in Table 6.6. With the additional dispersant, smaller d_p is obtained for Exp 2 and Exp 3; while the largest d_p is seen for Exp 1, likely due to the proportional relation between the dispersant and total surface coverage provided. As xylenes are present in the dispersant solution, the polarity of the initial reaction mixture slightly increases with the increased amount of added dispersant. This should lead to better solubility of the core polymer in the continuous phase that leads to larger d_p, according to literature.[10] However, the influence is small, and the increased dispersant amount (hence greater incorporation of the reactive dispersant with the core) has a much greater impact on the final particle size.

It should be noticed that, even with high mass ratio (≥ 0.5) between the dispersant and core polymer, significantly larger particles are produced in the batch system (Exp 1 in Table 6.5) than those produced in the semi-batch system (68.3 nm, Table 5.4). Heptane, xylenes and MA monomer are the initial solvent mixture for the batch system while the first two ingredients ($\delta_{heptane/xylenes}$ = 16.23, see Table 6.8) are the solvents for the semi-batch, with higher affinity between the polymer (pMA and pBMA) and heptane/xylenes mixture noticed in the second system. The correlation between d_p and δ in the two processing systems may be explained with the difference on reaction kinetics and particle nucleation period during the reaction. The initial [MA]/[Macromer] ratio is high in the batch system; thus reducing the probability of macromer incorporation in the early stages of reaction and leading to the formation of larger particles. The lower [MA]/[macromer] ratio in the semi-batch system favors macromer incorporation (compared

to the batch system), leading to better stabilization and formation of smaller particles. In addition, the total particle number probably stays constant shortly after the polymerization starts and the growth of particles by the absorption of monomer, oligomers and stabilizer until the monomer is consumed in the batch system;[12] however, formation of the new nuclei (precursor particles) may occur in the semi-batch system as monomers are gradually introduced, leading to the increased number of particles during the entire reaction.

Table 6.6 The correlation between HSPs of the dispersion systems and average particle size in batch production of NAD with an MA core and dispersant M2.

Sample	Dispersant amount[a)]	d_p (nm)	δ_{system}
Exp 1	1 (base)	610	15.99
Exp 2	1/3 more	220	16.04
Exp 3	2/3 more	135	16.09

a) Higher amount of dispersant was introduced to Exp 2 and Exp 3.

Table 6.7 Hansen solubility parameters of homopolymers.

Sample	δ_d[a)]	δ_p[a)]	δ_h[a)]	δ
pHEMA	17.1	5	12.1	21.5
pST	18.7	0.6	2.1	18.8
pMMA	16.2	1.6	4.7	16.9
pGMA	17.4	4.5	5.1	18.7
pMAA	17	3.4	12.6	21.4
pHEA	17.7	8.4	16.6	25.7

a) Data from HSPiP software and units are $MPa^{1/2}$.

Semi-batch systems are more complicated than batch, as fresh monomers (and dispersant) are introduced during the entire reaction period; thus, new particles may be formed during the entire feeding period. In order to simplify the calculation steps of the solvent parameters as applied to NAD systems, some assumptions are made. The contribution of the monomers to the HSP of the solvent mixture is neglected, as the instantaneous conversion is high in the starved-feed process. It is assumed that HSP values of homopolymers are representative of the lower-MW macromers used as dispersants. Hansen solubility parameters of the homopolymers are listed in Table 6.7, with the highest and lowest values seen for pHEA (most polar polymer) and pMMA (least polar polymer), respectively.

Table 6.8 Hansen Solubility parameters calculated for solvent mixture, macromers and core compositions.

	Sample	δ_d	δ_p	δ_h	δ
Solvent mixture	heptane/xylenes	16.2	0.4	1.1	16.23
Macromer	BMA[a)]	16.1	1.4	3.5	16.5
	BH5	16.15	1.58	3.93	16.7
	BH10	16.2	1.76	4.36	16.9
	BH15	16.25	1.94	4.79	17.1
MA dominated core	A	17.4	4.3	6.5	19.1
	AX	17.5	4.3	6.8	19.2
	ASX	17.6	3.9	6.4	19.1
	ASHX	17.6	4.3	7.4	19.6
	AS	17.5	3.9	6.1	19.0
	AHX	17.4	4.7	7.7	19.6
MMA/MA dominated core	B	16.6	2.5	5.3	17.6
	BX	16.7	2.6	5.7	17.8
	BSX	16.9	2.5	5.3	17.9
	BSHX	17	3	6.5	18.5

a) The pBMA homopolymer represents the BMA-type macromer.

Calculation of the solubility parameter for the mixed solvents, copolymer dispersants, and copolymer cores was again via the root-mean-square volume weighted average of δ of the solvents and the homopolymers, with the calculated values of the solvent mixture, macromers and core compositions summarized in Table 6.8. Let us first look at the influence of adding HEMA to the dispersant. Although the application of BH10 and BH15 to produce NAD in our current system was not successful, it is still valuable to investigate these trends, as more polar solvent (like ethyl acetate described in the patent[1]) can be introduced to improve the affinity between the macromer with functional hydroxyl groups and the medium. As the fraction of HEMA is increased in the BMA/HEMA macromer, the HSP increases away from the value for the heptane/xylenes mixture and closer towards the HSP values of the core polymers. The lowered affinity between dispersant and the continuous phase may explain the poorer performance of BH10 and BH15 as stabilizer in the system. The result also suggests that some improvements might be made by increasing the polarity of the solvent mixture. However, the solubility parameter for dispersant BH15 is approaching that of the MMA/MA copolymer ("B" in Table 6.8), indicating that it may be difficult to stabilize an MMA-containing core with a HEMA-containing macromer.

The other aspect investigated using HSP is the changing polarity of the core with composition. It is clear that pMA is more polar than pMMA, resulting in a larger difference in HSPs compared to the solvent mixture. Figure 6.6 shows the effect of the core composition on the average particle size for the NADs prepared with BH5 with all dispersant added initially, the results presented in this chapter. As the initial reaction conditions (heptane and dispersant amounts) remain the same, only the variation in core composition should contribute to the different NAD properties obtained. Thus, the final particle size is plotted as a function of the Hansen solubility parameter of the core polymer. The average values of d_p produced with MA dominated core are generally smaller than that prepared with MMA/MA dominated core. The

HSP of the MMA/MA dominated core is much closer to that of the solvent, which may explain the previous observation in Section 6.3.3 that NAD properties are more sensitive to core composition compared to the MA dominated system; as seen in the literature, the variation in particle size with recipe conditions becomes smaller as the difference in solvent and polymer HSP is increased.[8] However, the chain transfer reaction between MMA and the macromers should not be neglected as a factor complicating the correlation between d_p and δ of the core, since the macromers react less effectively with the addition of methacrylate to the core (see Chapter 4).

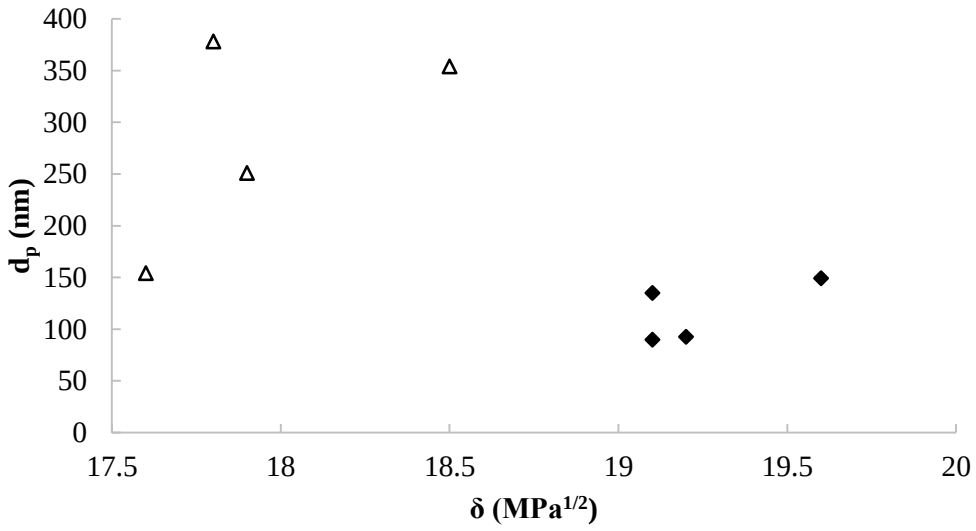

Figure 6.6 The correlation between the particle size and HSP of the core compositions: MA dominated core (closed symbols) and MMA/MA dominated core (open symbols). The new feeding method was applied to prepare the NADs.

Table 6.9 shows the RED numbers for the dispersant and core homopolymers in heptane/xylenes mixture. It is obvious that the lowest value is seen for pBMA, the polymer representing the BMA-type macromer, indicating a better affinity between the dispersant and medium. The numbers for pST and pMMA, monomers used in the core compositions, are higher.

As a qualitative methodology to evaluate the affinity between the core polymer and the solvent, the RED number required for the production of a stable NAD is less clear. In addition, RED for our copolymer core is not included due to the lack of relevant parameters. However, it is a reasonable hypothesis that the RED number may be higher than those listed in Table 6.9 when MA and HEMA are present, due to the decreased affinity between the core and the medium.

Table 6.9 RED numbers of dispersant and pure homopolymer in heptane/xylenes mixture.

Homopolymer	R_o [a)]	R_a [a)]	RED	Ref.
pST	12.7	5.1	0.40	[7]
pMMA	8.59	3.8	0.44	[7]
pBMA	8.5	2.6	0.31	[13]

a) Units are $MPa^{1/2}$.

Finally, an examination of the correlation between particle size and the solubility parameters of the core compositions may be worth the effort, comparing the BMA-type macromers to grafted Dispersant II using the standard feeding method. The same general conclusion can be made, as smaller particles are made with the MA-rich core compared to the MMA/MA core (lowest δ value) for all three of the dispersants, as plotted in Figure 6.7. However, these NAD systems may be more complicated than those discussed previously since the dispersant was gradually added to the reaction, leading to an increasing portion of xylenes in the heptane/xylenes mixture with time. In addition, the vinyl concentration of the macromer and grafted dispersants also influences the particle size, with discussions presented in Chapter 4. From Figure 6.7, the sensitivity of the particle size seems to increase with the higher vinyl concentrations, as the highest variation is seen for NADs prepared with M2.

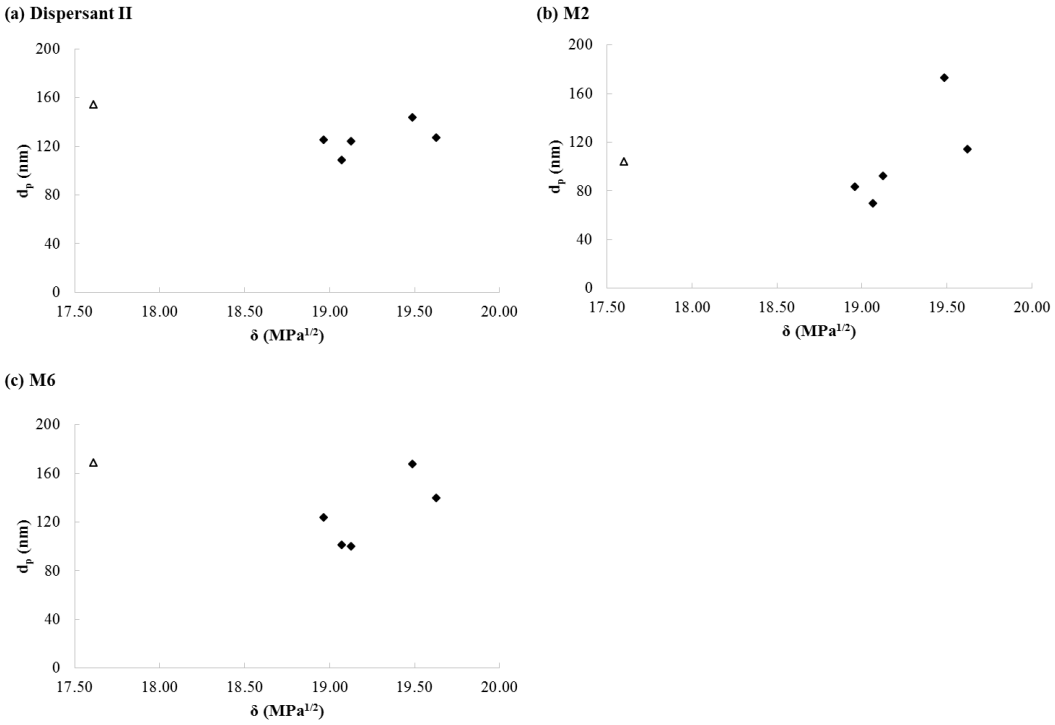

Figure 6.7 The correlation between the average particle size and the HSP of the core compositions: (a) Dispersant II; (b) M2; and (c) M6. MMA/MA copolymer (open symbol) and MA dominated core compositions (closed symbols). The standard feeding method was conducted for the NADs.

6.4 Conclusions

Stable NAD systems were produced only with the lowest (5%) hydroxyl content BMA/HEMA macromer. NADs made with an MA dominated core and the new feeding method seem to have a better performance in the presence of ST and HEA (more complex core), as small particles (< 150 nm) and low viscosity (< 300 cP) are obtained. For the less complex core, high viscosity is normally seen for the MA homopolymer and cross-linked MA formulations. NADs prepared with the HEMA-containing macromer and the MMA/MA dominated core have much larger particles (150-380 nm) and are highly viscous.

The use of Hansen solubility parameters to qualitatively explain the NAD systems, while preliminary, looks promising as a new tool to match solvent choices to core compositions and tune reaction conditions to produce stable NADs to fit different product application needs.

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Chapter 7

Conclusions and Recommendations

7.1 Conclusions

Non-aqueous dispersion polymerization has been conducted with acrylates, methacrylates, and styrene to produce 80-200 nm polyacrylic particles in aliphatic hydrocarbon solvents at high solids content through semi-batch procedures. The dispersions contain 60 wt% polymer and 40 wt% solvent, with the polymer component consisting of 65 wt% core polymer, assumed to be mainly in the particle phase, and 35 wt% of functionalized polymeric dispersant added to the solution. The solvent fraction is a mixture of 70 wt% heptane and 30 wt% xylenes, with the xylenes entering the reactor as solvent for the dispersant. The main requirements for the application of these dispersions as a component of non-aqueous coatings formulations, small average particle size (less than 150 nm) and low viscosity (< 500 cP), are achieved for most of the recipes investigated in this study, with various dispersants, core compositions and feeding strategies of the dispersant. A series of characterization methods were developed to quantitatively evaluate the NAD properties using ^{1}H NMR, SEC, Zeta-Sizer and Brookfield Viscometer.

The investigation started by developing simplified recipes to produce a grafted dispersant according to patent processes; the radical polymerization procedure used leads to a random distribution of the double bonds (introduced by an amino-catalyzed reaction of GMA with MAA units in the polymer) along the chain; with a low target dispersant chain length (DP of 20-30), many of the dispersant molecules may have more than one vinyl group, while a significant fraction of chains contains no functionality.[1] Without the unsaturated groups, only physical adsorption of the dispersant can occur. Thus, the largest particles in the NAD system are synthesized when the grafted dispersant contains no functionality due to a low portion of

dispersant incorporated to the core particles. Grafted dispersant with the highest vinyl group content suggests that multiple vinyl groups per chain can lead to multiple attachments of dispersant to the particles, leading to some cross-linking and also decreasing its effectiveness. Thus, the level of functional groups introduced to the grafted dispersant needs to be carefully controlled in order to synthesize stable NAD product with small particles and low viscosity. Under these conditions, however, a significant fraction of the dispersant is not utilized due to the lack of functionality on the shorter chains.

The limitations of the grafted dispersant led to a comprehensive study of using controlled vinyl-terminated BMA-type macromers as dispersant. Compared with the performance of the grafted dispersant, the macromers were more effective, exhibiting higher levels of incorporation and leading to smaller NAD particles produced with both MA homopolymer and MMA/MA copolymer cores. Smaller particles and better utilization of dispersant was observed for NADs prepared with lower MW macromers, a result of the higher vinyl concentration per unit mass. However, the incorporation of dispersant for production of the MMA/MA copolymer particles remained around 40%, a result explained by literature that describes that methacrylate macromers do not homopolymerize and thus undergo β-scission when encountering a methacrylate radical; it is only by reacting with an acrylate radical that the macromer is incorporated into the core polymer. Thus, better incorporation (as high as 70%) and smaller particles are seen for all NADs produced with an MA homopolymer core utilizing the macromer dispersant as compared to the MMA/MA copolymer products.

Based upon the above findings, the influence of changing the core composition on the NAD performance was systematically investigated using both the grafted and two of the macromer dispersants. In all cases, adding ST, HEA, and cross-linker monomers led to increased particle size. ST lowers the NAD MW and leads to the lowered efficiency of the stabilizers due to its slower polymerization rate[2] and the sterically hindered radicals[3] generated when it polymerizes

with macromer dispersant; a lower impact of HEA and cross-linker on the dispersion particle size and dispersant effectiveness is seen. In general, NADs made with grafted dispersant are less affected by the variation of the core formulations, compared to the NADs made with the macromer dispersants.

As found for the simpler recipes, the lower MW macromer showed a better ability to lower particle size per unit mass dispersant added. Thus, it was selected for the investigation of NAD particles containing up to 20 wt% HEA in the core. Small particles (< 135 nm) were obtained and NAD viscosity remained low, and these promising findings led us to explore the utilization of hydroxyl-group functionalized macromers. In addition, a new strategy for adding the dispersant (all added before the polymerization) demonstrates the potential of simplifying the current semibatch feeding strategy used industrially, as small particles and high dispersant efficacy are maintained.

The final extension of the system studied was the utilization of BMA/HEMA macromers to produce MA dominated and MMA/MA dominated copolymer cores in order to introduce cross-linkable moieties into the dispersant. However, only the macromer with the lowest HEMA content (5%) led to a stable dispersion. The more complex core compositions benefit the NADs with the MA dominated core and the copolymer dispersant, as the viscosity drops significantly while small particles are still obtained. However, the MMA/MA dominated core compositions have a greater impact on the NAD products made with the BMA/HEMA macromer, as much larger particles (some > 300 nm) were formed, along with very viscous dispersions (> 2000 cP). The unsuccessful application of macromers with higher HEMA fractions (10% and 15%) motivated the preliminary study of applying Hansen solubility parameters to interpret the complex semibatch system, and as a potential methodology for matching the selection of the core and the solvent composition in the future.

7.2 Recommendations for Future Work

7.2.1 Recommendations for the Experimental Work

Grafted dispersant with randomly distributed vinyl groups is less efficient than the macromer dispersant in stabilizing the non-aqueous dispersion systems. Design of a BMA/MAA type block copolymer produced through controlled polymerization (ATRP or RAFT) would be interesting to pursue. The BMA block can be produced first, followed by a controlled number of MAA units added as the second block. The acid groups can then be reacted with GMA to form the reactive vinyl groups. In this way, the vinyl groups will be located on every chain (assuming good control and livingness during polymerization to maintain block purity) near the terminal position. This design combines the controlled functionality of the macromer dispersant with the higher reactivity of the grafted vinyl groups, which should make the dispersant more effective.

The addition of more polar solvents, such as ethyl acetate and isopropanol, may be introduced to the current heptane/xylenes mixture to increase the affinity between the solvent medium and the BMA/HEMA type macromers. This modification may allow the application of macromer with a higher HEMA content to make stable NADs. In addition, lower MW BMA/HEMA macromer may be also good for the stability, by increasing the vinyl concentration in the system.

As for the core composition, the MMA/MA ratios can be systematically varied, to determine the fraction of methacrylate in the recipe that can be tolerated with the macromer dispersant.

7.2.2 Recommendations for Study of Solubility Parameters

Hansen solubility parameters have been investigated as an approach to qualitatively understand the nucleation of the particles and control of particle size. Combining this treatment

with Flory-Huggins model,[4] group-contribution principles,[5] or Teas graph[5] may lead to a more quantitative methodology to design appropriate core-medium systems. For example, Equation 7.1 describes the Flory-Huggins model in terms of the activity coefficient for a binary system,[4]

$$ln\gamma_1 = ln\frac{\phi_1}{x_1} + 1 - \frac{\phi_1}{x_1} + \chi_{12}\phi_2^2 \qquad (7.1)$$

where γ_1 is the activity coefficient; x and ϕ are the volume and molar fractions; χ_{12} is the composition independent Flory-Huggins interaction parameter;[6] 1 and 2 represent the solvent and the polymer, respectively. Combination of the Flory-Huggins model with Hansen Solubility Parameters results in Equation 7.2,[4]

$$\chi_{12} = \alpha\frac{v_1}{RT}[(\delta_{d,1} - \delta_{d,2})^2 + 0.25 \times (\delta_{p,1} - \delta_{p,2})^2 + 0.25 \times (\delta_{h,1} - \delta_{h,2})^2] \qquad (7.2)$$

where α is the correction constant set to 1 if the dispersion force is the dominated force and v_1 is the molar volume of the solvent. A χ_{12} value of less than 0.5 predicts that the polymer will be completely miscible in the solvent; this criterion may be applied to select a solvent mixture (or dispersant composition) to ensure good compatibility of the two, while checking the incompatibility between the core polymer and the solvent.

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Appendix

A.1 Preliminary Study on Reaction Conditions of Grafted Dispersant (Chapter 3)

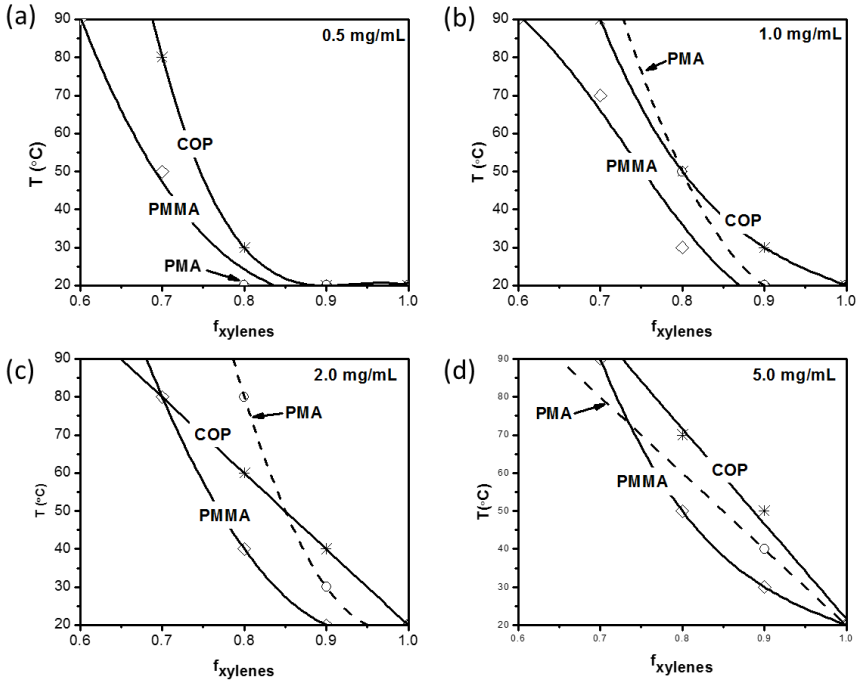

Figure A.1.1 Solubility of pMMA, pMA and p(MMA-co-MA) oligomers with similar number-average molecular weight at varied concentrations as a function of weight fraction of xylenes in the solvent mixture ($f_{xylenes}$) and temperature: (A) 0.5mg/ml, (B) 1mg/ml, (C) 2mg/ml, and (D) 5mg/ml. The points represent the solubility limit of pMMA oligomer at specific xylenes weight fraction and temperature; while, the oligomers are soluble above the fit lines.

A.2 Investigating the Effectiveness of Reactive Dispersants in Non-Aqueous Dispersion Polymerization (Chapter 4)

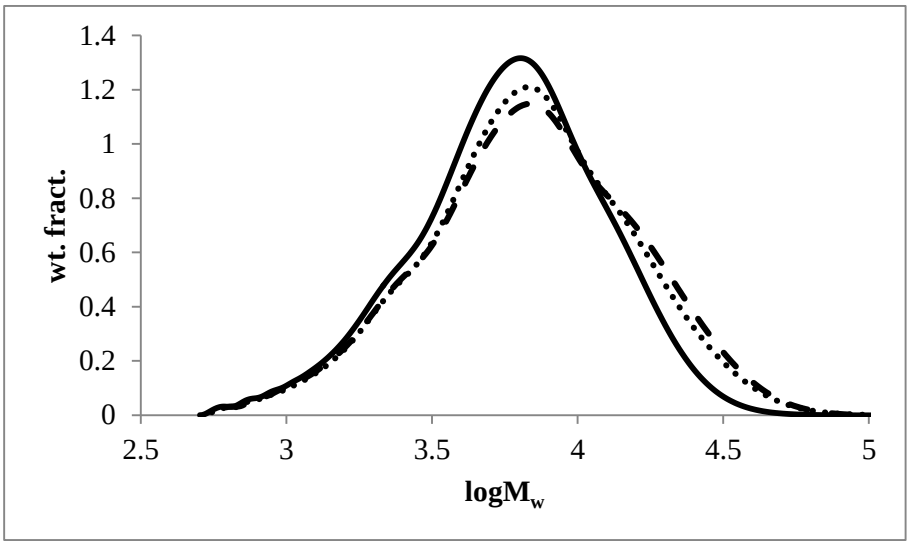

Figure A.2.1 MMDs of grafted dispersants produced with different levels of functionalization, as controlled by the molar ratio of GMA added to MAA units in the polymer chain: Dispersant I with GMA/MAA=0 (solid line), Dispersant II with GMA/MAA=0.5 (dashed line) and Dispersant III with GMA/MAA=1.0 (dotted line).

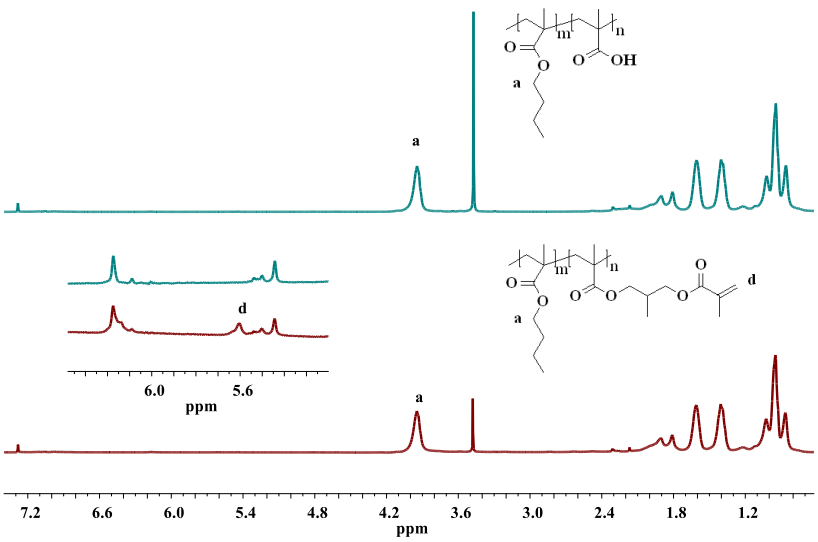

Figure A.2.2 ^{1}H NMR Spectra of Dispersant III: before the addition of GMA (top) and after functionalization with GMA (bottom). The peak labelled "d" indicates successful incorporation of reactive vinyl groups to the dispersant.

The weight fraction of soluble polymer recovered from the NAD system after destabilization with additional heptane is calculated by the following equation:

$$w_{sp} = \frac{\frac{w_1}{(1-w_1)} \times (m_1 \times w_s + m_2)}{m_1}$$

where w_{sp} is the weight fraction of soluble polymer in the dispersion, w_1 is the weight fraction of polymer after centrifugation in a sample vial, m_1 is the mass of the NAD sample, m_2 is the mass of heptane added before centrifugation, and w_s is the weight fraction of solvent in NAD samples.

The soluble polymer is composed of two components: unreacted dispersant remaining in the continuous phase and also soluble short chain length p(MMA/MA) copolymer or pMA homopolymer, depending on the core composition formed during the polymerization. The weight fraction of free dispersant is thus corrected for the presence of soluble "core" polymer by using NMR, specifically the molar ratio between the p(BMA) –CH_2– group (~3.9 ppm in Figure A.2.3)

and the p(MMA/MA) –CH_3– group (at ~3.45-3.6 ppm in Figure A.2.3 and Figure A.2.10, respectively). After this adjustment, $w_{inc.}$, the fraction of dispersant incorporated to the particle phase is calculated as:

$$w_{\text{inc}} = 1 - \frac{w_{\text{d}}}{w_{\text{int}}}$$

where $w_{int.}$ is the initial weight fraction of dispersant in the NAD composition. It is assumed in the calculation that the monomer conversion during NAD polymerization was 100%, as is verified by gravimetry.

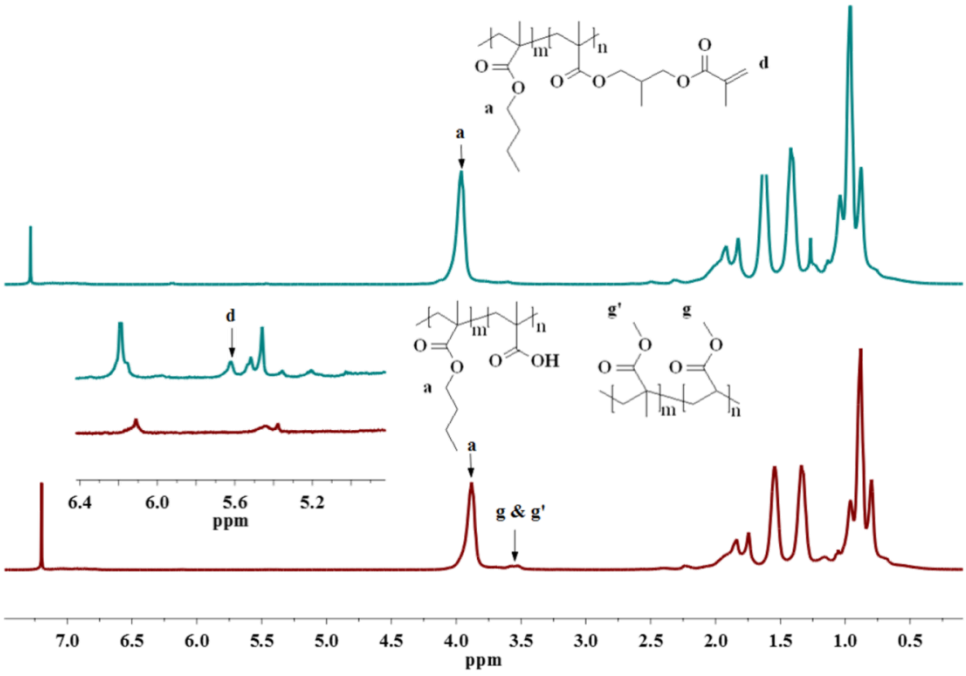

Figure A.2.3 ^{1}H NMR Spectra of Dispersant II (top) and soluble polymer recovered from NAD II (bottom). No vinyl groups can be seen in the soluble polymer fraction (disappearance of peak d), indicating that the polymer remaining in solution is not functionalized. Peak a is the methylene group attached to the ester group of pBMA, while peaks g and g´ are from the methyl group bonded to the ester group of pMA and pMMA, respectively.

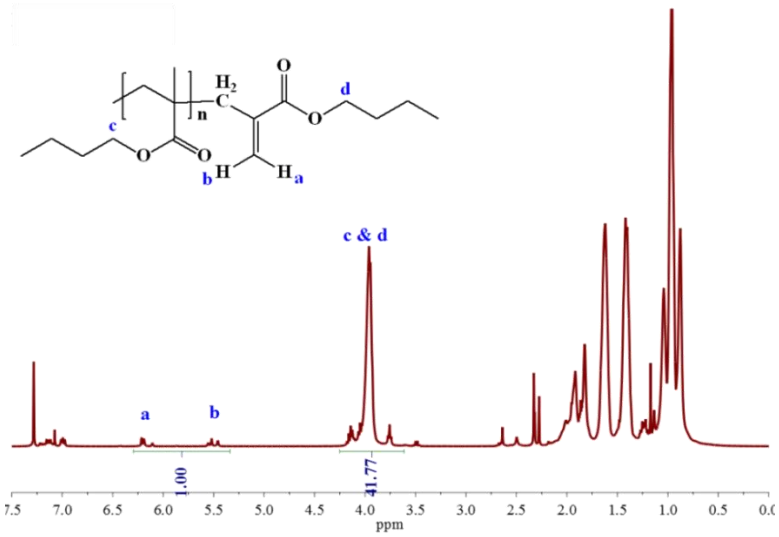

Figure A.2.4 ^{1}H NMR spectrum of pBMA macromer M1. Chain-length is calculated by the ratio between the area of peaks c & d (methylene group bonded to the ester) and the areas of a & b (vinyl-terminated group). Chain length of M1 is 40 (M_n equals to 5688 Da), which is close to the result (M_n = 5269 Da) measured by SEC with polystyrene calibration.

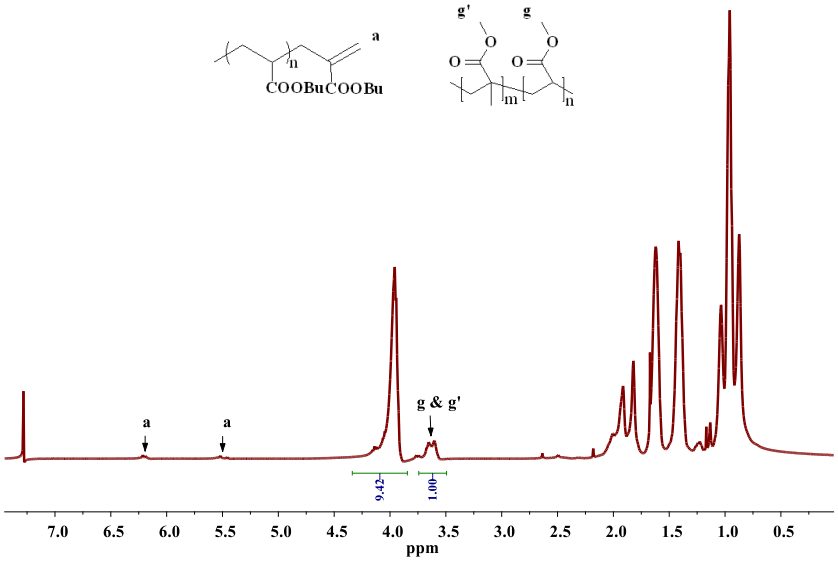

Figure A.2.5 ^{1}H NMR of soluble polymer recovered from NAD B-M2. Vinyl double bonds can still be detected (peak a), indicating incomplete macromer conversion. As discussed in

Figure A.2.3, peaks g and g´ result from soluble p(MA-co-MMA) formed during the reaction.

The number of particles in the system can be estimated by combining the measured average particle size data (Figure A.2.6) with the known amount of monomer fed to the system and measured monomer conversion:

$$N_{\mathrm{p}} = \left(\frac{xm}{\rho \frac{\pi}{6} {d_p}^3} \right) \left(\frac{1}{V_{\mathrm{r}}} \right)$$

where N_{p} is the number of particles per liter, x is the fractional monomer conversion, m is the mass of monomer added to the system (up to time t), d_{p} is the average particle diameter, and V_{r} is the total reaction volume (also increasing with time). The average density ρ is calculated assuming the particles consist entirely of polymer when diameter is measured by light scattering. Within experimental scatter, there is no obvious increase in the concentration (number/L) of particles after 120 minutes (Figure A.2.6). However, when accounting for the increase in reactor volume due to semibatch feeding up to 210 min, the total number of particles in the system increases (Figure A.2.8).

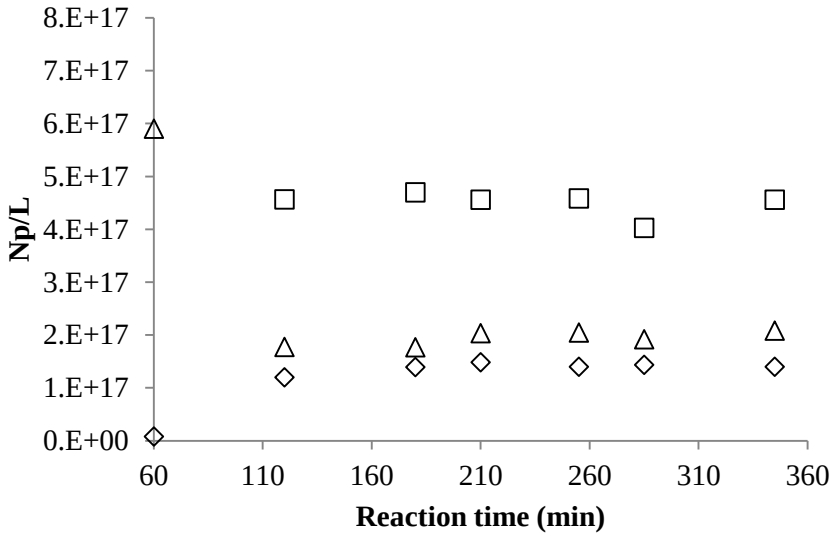

Figure A.2.6 The evolution of particle number (per L) during the semibatch production of NAD II (diamond), NAD B-M2 (square), and NAD B-M5 (triangle) reactions.

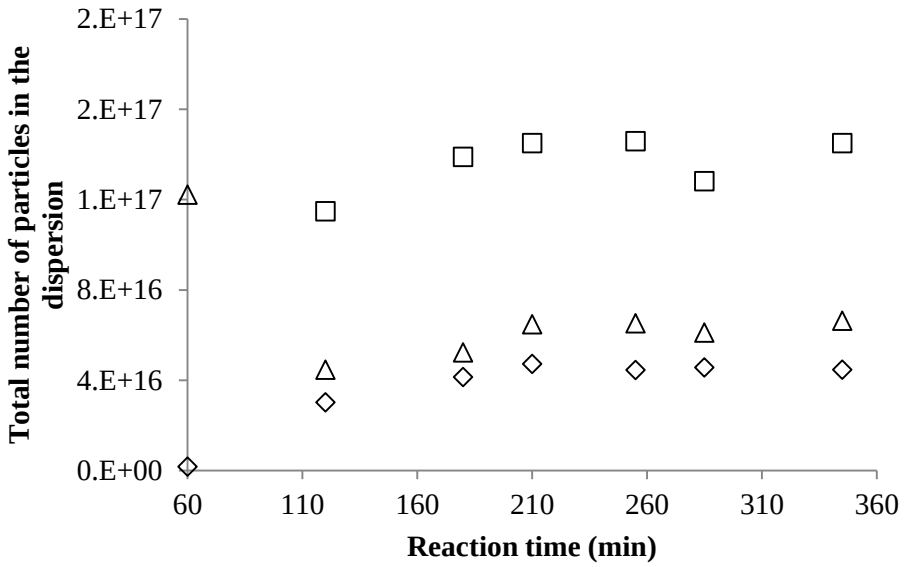

Figure A.2.7 The evolution of total number of particles in the NAD systems during the semibatch production of NAD II (diamond), NAD B-M2 (square), and NAD B-M5 (triangle) reactions.

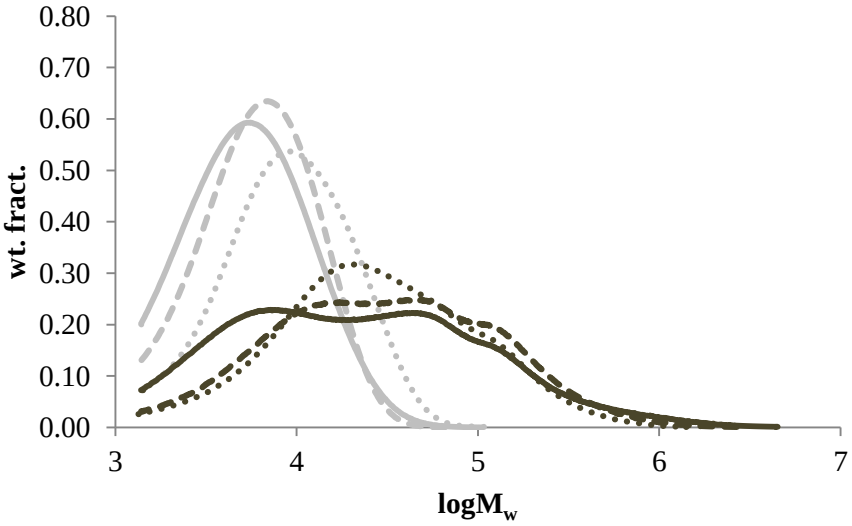

Figure A.2.8 Polymer MMDs of dispersants (grey lines) and the corresponding product produced by non-aqueous dispersion (NAD) polymerization (black lines): Dispersant

II/NAD A-II (solid lines), Dispersant M2/NAD A-M2 (dashed lines) and Dispersant M6/NAD A-M6 (dotted lines).

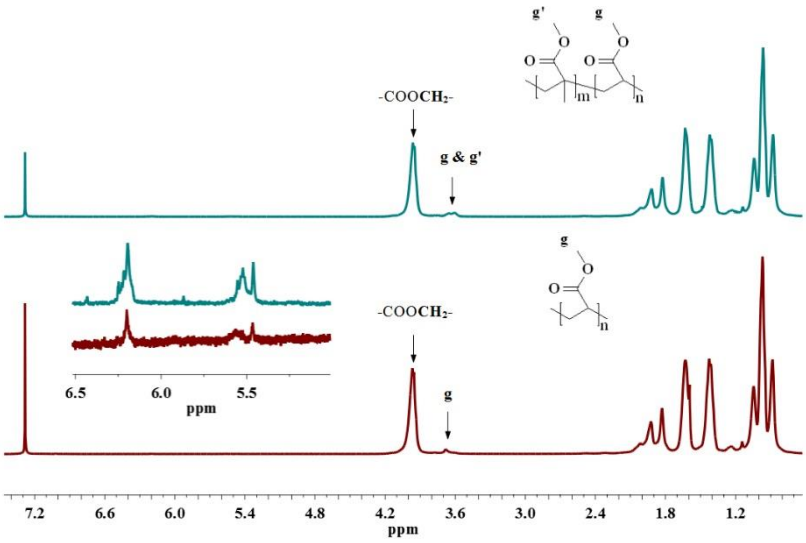

Figure A.2.9 ^{1}H NMR Spectra of soluble polymer recovered from the NADs: soluble polymer of NAD B-M6 (top) and soluble polymer of NAD A-M6 (bottom). The lower concentration of reactive double bonds remaining in solution in the acrylate homopolymerization case is evident.

A.3 The Influence of Core Composition and Reaction Conditions on NAD Properties (Chapter 5)

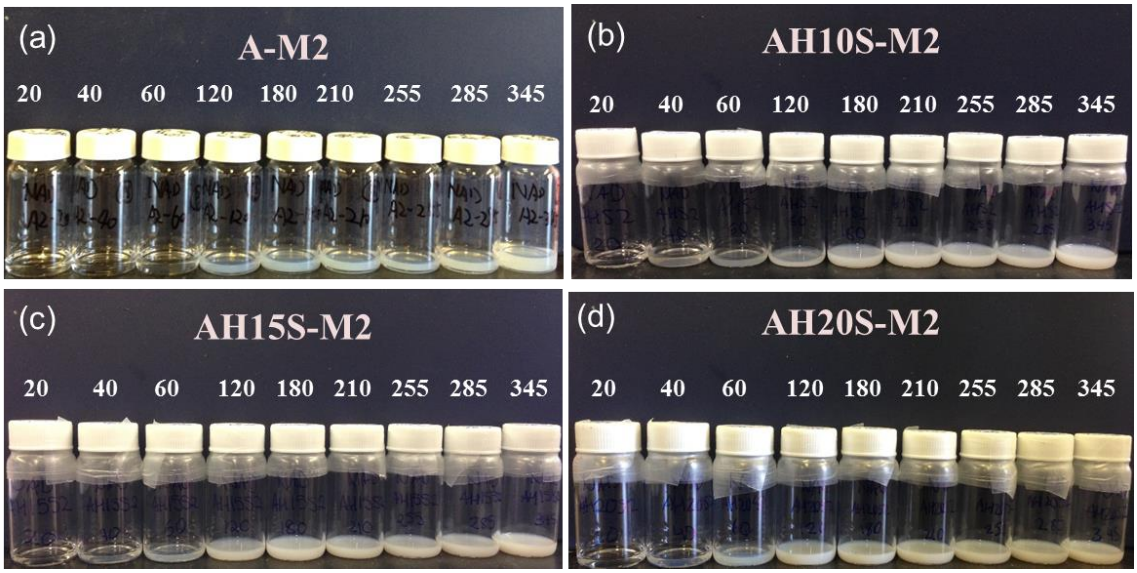

Figure A.3.1 Images of NADs prepared with M2 and higher HEA content in the core compositions: (a) NAD A-M2, (b) NAD A10HS-M2, (c) NAD AH15S-M2, and (d) NAD AH20S-M2.

Table A.3.1 Reproducibility of NADs made with similar M_w macromers

	M2		NAD					
Sample	M_n (Da)	M_w (Da)	M_n (Da)	M_w (Da)	w_{inc}	d_p (nm)	PdI	η (cP)
Exp 1	5600	9200	16000	81500	0.61	70	0.06	199
Exp 2	4500	8200	16526	91500	0.62	73	0.05	490

A.4 Investigation of Macromer Dispersant with Hydroxyl Groups (Chapter 6)

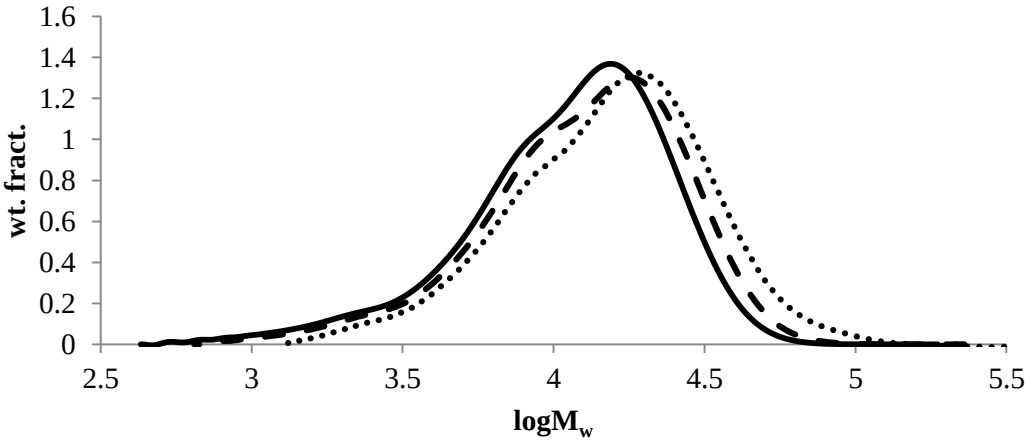

Figure A.4.1 MWDs of BH5 (solid line) and soluble polymer recovered from NAD FASX (extracted by H8X2, dashed line) and FAX10 (10 wt% cross-linker, extracted by xylenes, dotted line).