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Design of acrylic dispersants for non-aqueous dispersion polymerization: the importance of thermodynamics

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Please submit a plain text version of your cover letter here. Please note, if you are submitting a revision of your manuscript, there is an opportunity for you to provide your responses to the reviewers later; please do not add them to the cover letter.	Dear Stefan, Attached is another contribution from my group for publication in MRE. It describes some of our work with dispersion polymerization: the first paper in our study was also published in MRE two years ago, and the second paper published in React. Funct. Polym. Potential reviewers include Joserra Leiza (University of the Basque Country), John Tsavalas (University of New Hampshire), and Enrique Saldivar (CIQA).
Do you or any of your co-authors have a conflict of interest to declare?	No. The authors declare no conflict of interest.

Design of acrylic dispersants for non-aqueous dispersion polymerization: the importance of thermodynamics[a]

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Poly(acrylic) nanoparticles (NP) produced by non-aqueous dispersion (NAD) radical polymerization are important components in many automotive coating formulations. A series of experiments show that the properties of final dispersions (particle size distribution, viscosity and stability) correlate to the thermodynamics of the NAD system, as characterized by solubility parameters and solubility distances among the continuous phase, the soluble polymeric dispersant, and the polymer particles. The insights gained have enabled the design of a macromonomer dispersant containing greater than 10 mol% 2-hydroxyethyl methacrylate (HEMA), a necessary functional comonomer addition for end-use properties. Stable NAD products were synthesized by changing the principal component of the dispersant from butyl methacrylate (BMA) to 2-ethylhexyl methacrylate (EHMA).

Supporting Information is available online from the Wiley Online Library or from the author.

1. Introduction

Polyacrylic nanoparticles produced by radical dispersion polymerization have been used since the 1960s as a component in solvent-based automotive topcoat and basecoat coatings to reduce both system viscosity at high solids content (>50 wt%) and the energy required for curing.[1] A non-aqueous dispersion (NAD) system consists of three components: non-soluble polymeric nano-sized particles (<200 nm), a hydrocarbon continuous phase, and a soluble steric dispersant to stabilize the particles. Compared with the soluble polymer components in the formulation, the NAD nanoparticles have much higher molecular weight (MW) and can be uniformly cross-linked into the final coat without affecting optical clarity.[2]

The dispersion polymerization process starts as a homogenous system with monomers, initiator and lower-MW polymeric stabilizer all soluble in the medium (aqueous or non-aqueous). When reaction commences, the newly-generated polymer radicals precipitate when they reach a critical chain length, as the solvent is chosen so that the polymer formed has poor solubility in the medium; at this point the system becomes heterogeneous as the chains precipitate to nucleate particles. The choice of the dispersant and solvent is very important for successfully controlling the polymer particle size and particle size distribution, as well as the viscosity of the dispersion. Numerous studies of dispersion processes examine the polymerization of non-polar monomers conducted in water[3] or in a mixture of water and short-chain alcohols[4-11] to produce a narrow particle size distribution (usually in the 1-10 micron range) at relatively low polymer content, <20 wt%. Fewer studies are concerned with the dispersion polymerization of more polar monomers in non-aqueous medium such as dodecane, [12,13] hexane[14,15] and heptane,[16] again usually at relatively low solids content in a batch process. These synthesis conditions differ significantly from the semi-batch process used to produce polyacrylic NADs in a nonpolar solvent with average particle size of less than 200 nm at high solids content (>50 wt%).[17]

An essential component to control particle size during NAD polymerization is the dispersant, which stabilizes the more polar polymeric particles in the less polar solvent. Important characteristics include dispersant average chain-length and composition, and also its functionality. The low-MW material is designed to contain reactive double bonds, such that the dispersant chains become covalently bonded to the particles, aiding in stabilization.[2,17] The incorporation of the dispersant into growing chains affects both the nucleation and stabilization of particles. Past research in our group demonstrated that a poly(butyl methacrylate) (P(BMA)) macromonomer (Đ ~ 2), synthesized through radical polymerization with cobalt chain transfer (CCT) agent such that every chain contains a double bond at its terminus, is more effective than a P(BMA) dispersant with double bonds grafted at random positions among the chains. The latter material, typically used in industry,[2,17] is generated by reacting the epoxy group of glycidyl methacrylate (GMA) with the carboxyl group of methacrylic acid (MAA) groups incorporated in a copolymer consisting of predominantly butyl methacrylate (BMA) units; as such, the vinyl functionality is randomly distributed among the chains, rather than the controlled vinyl group positioned at the macromonomer chain end. Thus, graft dispersant can result in multiple attachments to the particle surface due to the uncontrolled placement of vinyl groups among the dispersant chains, while macromonomer dispersant is likely to extend from its anchoring point on the particle into the solvent, providing superior stabilization.

While the macromonomer proved to be more effective than the grafted dispersant, producing smaller particles at equal loading, it was also found that the fraction of incorporated P(BMA) macromonomer significantly decreased when the composition of the polymer particle core was changed from pure methyl acrylate (MA) to methyl methacrylate/methyl acrylate (70/30 w/w MMA/MA).[2] This result was attributed to the reduced chemical reactivity of a methacrylate radical with the macromonomer, which acts as a chain transfer agent in the presence of MMA. Although the changes in particle size and size distribution were attributed to the differences in levels of incorporated P(BMA) macromonomer, in this work it will be shown that the relative compatibility among the particle core, dispersant and solution~~vent~~ also influence particle size and size distribution as the composition of the core is modified.

A second type of functionality added to the dispersant chains is hydroxyl groups, needed to crosslink the non-incorporated dispersant chains during the application of the coating. It was found that adding up to 10 mol% of 2-hydroxyethyl methacrylate (HEMA) as a comonomer to the P(BMA) macromonomer destabilized the final dispersion, although particle size was not greatly affected.[18] In this study, we show that this result can be attributed to the increased polarity that results from adding HEMA to the dispersant, upsetting the thermodynamic balance between solution~~vent~~, dispersant and particle. Thus, it is very important to systematically study the influence of the compositions of the particle core, dispersant and solvent on average particle size, particle size distribution, viscosity and stability of the final dispersion. We introduce Hansen solubility parameters and solubility distances to quantify the interactions between the three components, and use the insight gained to design a new macromonomer dispersant containing above 10 mol% HEMA that produces a stable final dispersion.

2. Experimental Section

2.1 Materials

The monomers *n*-butyl methacrylate (BMA, Sigma-Aldrich, 99%), methyl methacrylate (MMA, Sigma-Aldrich, 99%) and methyl acrylate (MA, Sigma-Aldrich, 99%) were used as received. The initiators, *tert*-butyl peracetate (TBPA, Sigma-Aldrich, 50 wt% in mineral spirits) and 2,2'-azobis-(2-methylbutyronitrile) (Vazo®67, E. I. du Pont), were used without any further purification. Mixed xylenes (Fisher Scientific, ≥ 98.5%), p-xylene (anhydrous, Sigma-Aldrich, 99%), heptane (anhydrous, Sigma-Aldrich, 99%), deuterochloroform ($CDCl_3$, Sigma-Aldrich, 99.8 atom% D) and butyl acetate (Sigma-Aldrich, 99%) were used as received.

P(BMA) and poly(2-ethylhexyl methacrylate) (P(EHMA)) based macromonomers containing varying levels of HEMA comonomer were kindly supplied by Axalta Coating Systems as 60 wt% polymer solution in xylenes, synthesized through ~~free~~ radical ~~and~~ cobalt chain transfer polymerization.[19] Table 1 summarizes the number-average (M_n) and weight-average (M_w) MWs of the macromonomers, with the full molecular weight distributions (MWDs) determined by size exclusion chromatography (SEC) presented in Figure 1. M_n values were maintained between 6000 and 7000 Da, with M_w between 10000 and 12000 Da. Terminal double-bond functionality was verified by NMR, as previously documented.[2,18]

Table 1. Molecular weight averages of P(BMA) and P(EHMA) based macromonomers, both homopolymers and copolymers with 2-hydroxyethyl methacrylate (HEMA).

Macromonomers	M_n [a] **[Da]**	M_w **[Da]**	**Đ**
P(BMA)	6000	10200	1.70
P(BMA) (5 mol% HEMA)	6100	11100	1.82
P(BMA) (10 mol% HEMA)	6000	11200	1.87
P(EHMA)	6000	9800	1.63
P(EHMA) (8 mol% HEMA)	6600	11500	1.74
P(EHMA) (16 mol% HEMA)	6900	11900	1.72
P(EHMA) (24 mol% HEMA)	7000	11600	1.66

[a] Number and weight average molecular weights based on PS standard calibration.

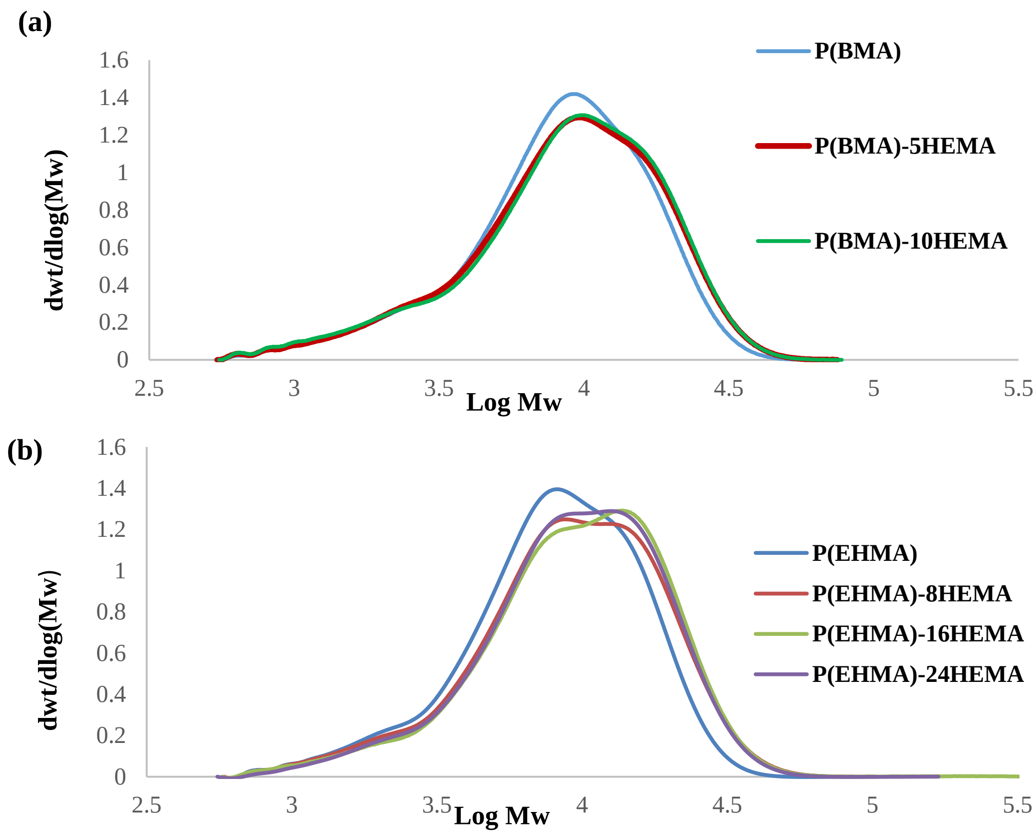

Figure 1. Molecular weight distributions of dispersants: (a) P(BMA) based macromonomers; (b) P(EHMA) based macromonomers.

2.2 Preparation of Non-Reactive P(BMA) Dispersant *via* Solution Polymerization

A low MW P(BMA) dispersant (with no terminal double bonds) was prepared by radical polymerization in order to compare its stabilizing power to that of the reactive macromonomers. The semi-batch synthesis procedure was identical to that outlined by Yang and Hutchinson,[2] scaled to a 700 mL reactor. Xylenes (128.7 g) were added to the reactor and heated to 138℃. A mixture consisting of 294.5 g BMA, 48.5 g xylenes and 16.2 g TBPA solution was then pumped to the reactor at a constant rate over 240 min, with the mixture held at ~~constant temperature~~138 ℃ for an additional 120 min. The fractional monomer conversion was 92.5% according to ^{1}H NMR, with no observable influence of a gel-effect, as viscosity remains low in the high temperature, low-MW polymer system. The polymer was purified by adding 10 g of the dispersant solution into a glass vial with 10 mL methanol/water, and chilled with iced water to aid precipitation. The upper phase (mainly solvent/monomer) was decanted, with the remaining sample dried under vacuum at 110 ℃ for 24 h. The resulting P(BMA) contained less than 1% residual monomer, with MW values unchanged at M_n =7400 and M_w=13500 Da, indicating negligible loss of oligomers during the purification.

2.3 Non-Aqueous Dispersion Polymerization

Non-aqueous dispersion polymerizations were conducted to produce both MMA/MA copolymer and MA homopolymer as the particle core. The typical semi-batch reaction consisted of three steps. Initially 64.1 g dispersant solution (60 wt% polymer in xylenes) and 65.1 g heptane were charged to the reactor and heated to 92 ℃, followed by rapid addition of a pre-mixed solution of 2.15 g butyl acetate and 0.16 g Vazo®67. Secondly, a feed stream consisting of a mixture of 102.5 g pure MA (or 30/70 w/w MA/MMA), 24.35 g heptane, 32.2 g dispersant solution and 1.25 g Vazo®67 was fed at a constant rate over 210 min, with the reaction mixture then held at 92 ℃ for a further 45 min. Finally, 4.9 g butyl acetate and 0.42 g Vazo®67 were added at a constant rate over 30 min, with the reaction mixture held for a further 60 min before cooling to room temperature. Samples were taken throughout the reaction, as well as of the final dispersion. This procedure follows that established by Yang and Hutchinson[2] based upon an industrial patent.[17]

2.4 Quantification of Free Dispersant

The fraction of dispersant chemically anchored and physically adsorbed to the NAD particles was quantified from the difference between the known mass of dispersant added to the reaction and the mass of the free dispersant that remained in the continuous phase in the final dispersion. The procedure to quantify the latter value was adopted from previous work,[2,18] adding 2 g of the NAD mixture into a vial to which was added 3.4 g heptane. The mixture was centrifuged at 6,000 rpm for 10 min to separate the phase into a clear upper solution and a dense particle rich phase. A sample of the clear upper phase liquid was removed and weighed, with the amount of soluble polymer determined by gravimetry after taking the sample to dryness under vacuum. The absence of particles in the solution separated by centrifugation was verified using LS for dispersions produced with P(BMA) based dispersants; as discussed later, not all particles were separated applying this procedure to NADs produced with P(EHMA) dispersants. As this soluble polymer may also contain some P(MA) "core" polymer produced during the reaction, the value was corrected after measuring the molar ratio between free dispersant and soluble oligomer measured by ^{1}H NMR. This adjusted measure of the total dispersant remaining in the solution was used to calculate the weight fraction of incorporated dispersant (W_{inc}), defined as the mass of chemically anchored and physically adsorbed dispersant divided by the total mass of dispersant added. Further details of this calculation are described in the Supporting Information.

2.5 Characterization

^{1}H NMR was used to quantify both the final conversion of non-reactive dispersant and the composition of the soluble material in the continuous medium after NAD polymerization to calculate W_{inc}. Dried samples were dissolved in deuterated chloroform ($CDCl_3$) and analyzed using a Bruker Avance-400 MHz spectrometer following literature procedures.[2] Average molecular weights and molecular weight distribution of samples were measured by size exclusive chromatography (SEC) using a Waters 2960 separation module followed by a Waters 410 differential refractometer (DRI) operated at 35 ℃**,** with THF as eluent at a flow rate of 0.3 mL·min^{-1}. The DRI detector was calibrated by 10 narrow MWD polystyrene standards with MW from 870 Da to 355,000 Da.

Average particle size and size distribution were measured on a Malvern Nano ZS Zeta-Sizer using dynamic light scattering (DLS) with an angle of 173° at 25 ℃ in a quartz cuvette. A small sample of NAD mixture was ~~Samples were~~ diluted using a 50/50 v/v solvent mixture of heptane and p-xylene, with the refractive index (1.444) and viscosity (0.5000 cps) of the binary solvent mixture calculated by the Lorentz-Lorenz formula[20] and the Grunberg and Nissan equation,[21] respectively.

The viscosities of the NAD mixtures were measured at room temperature using a Brookfield Viscometer with a UL adapter. All of the reported values were obtained under a rotation rate of 1.0 rpm at 1 min after starting the viscometer.

3. Results and Discussion

3.1 The Importance of Thermodynamics in NAD Systems

It was previously shown that P(BMA) macromonomer is a more effective dispersant for the production of P(MA) homopolymer dispersions compared to dispersions of P(MMA-ran-MA) copolymer containing 70 wt% MMA; the P(MA) particles were of smaller size than the copolymers (90 *vs* 140 nm) and the fraction of dispersant incorporated was also higher (increased value of W_{inc}).[2] The explanation for this result was that P(BMA) macromonomer can react with an MA radical but acts as a chain transfer agent with an MMA radical. While this reactivity difference is of significant importance, there are also thermodynamic factors to consider, as P(MA) is more polar than P(MMA). Thus, we explore the influence of the core composition on NAD systems by performing reactions with a non-reactive P(BMA) dispersant in place of the reactive P(BMA) macromonomer. As summarized by Table 2, the molecular weight of P(MMA) dispersion produced in the presence of the non-reactive dispersant (E2) is significantly higher than that produced using the macromonomer (E1), confirming the role of the macromonomer as a powerful chain-transfer agent during methacrylate polymerization. Interestingly, however, neither of the P(MMA) dispersions were stable, with both reactions terminated after 1 h due to particle coagulation.

The importance of thermodynamics on the system was then tested by changing the composition of the NAD particle from P(MMA) (E2) to copolymer (E3) to P(MA) homopolymer

(E4), keeping the non-reactive P(BMA) as dispersant and all other conditions constant. Decreasing the fraction of MMA in the particle core brings stability to the system, with final average particle size lower for the P(MA) homopolymer compared to the copolymer. Furthermore, as shown in Figure 2, there is a change in the particle size distribution (PSD) from unimodal (MA homopolymer) to a bimodal distribution (copolymer) to an unstable system with coagulation (MMA homopolymer, showing PSD of coagulum-free material). These results obtained with a non-reactive dispersant indicate that the relative polarity of the particle core and solvent has a significant effect on NAD stability and particle size.

Table 2. Characteristics of dispersions produced with varying particle compositions in the presence of non-reactive and macromonomer P(BMA) dispersants.

Experiments	**Stability of dispersion**	**Particle d_p[c] [nm]**	**Particle size distribution**	**M_n[d] [Da]**	**Đ**
E1[a] (MMA core)	Not stable, stopped at 60 min	-	Bimodal, PDI = 0.466	9900	1.72
E2[b] (MMA core)	Not stable, stopped at 60 min	-	Bimodal PDI = 0.551	23700	1.93
E3[b] (MA/MMA core) (30/70 wt.)	Stable	310	Multimodal, PDI = 0.388	*n.d.*	*n.d.*
E4[b] (MA core)	Stable	175	Unimodal, PDI = 0.080	*n.d.*	*n.d.*

[a] Using macromonomer; [b] Using non-reactive dispersant; [c] d_p is the average particle size and PDI is the dispersity of the particle size distribution as measured by DLS; [d] Number average polymer molecular weight of NAD system using PS calibration. *n.d.* = not determined.

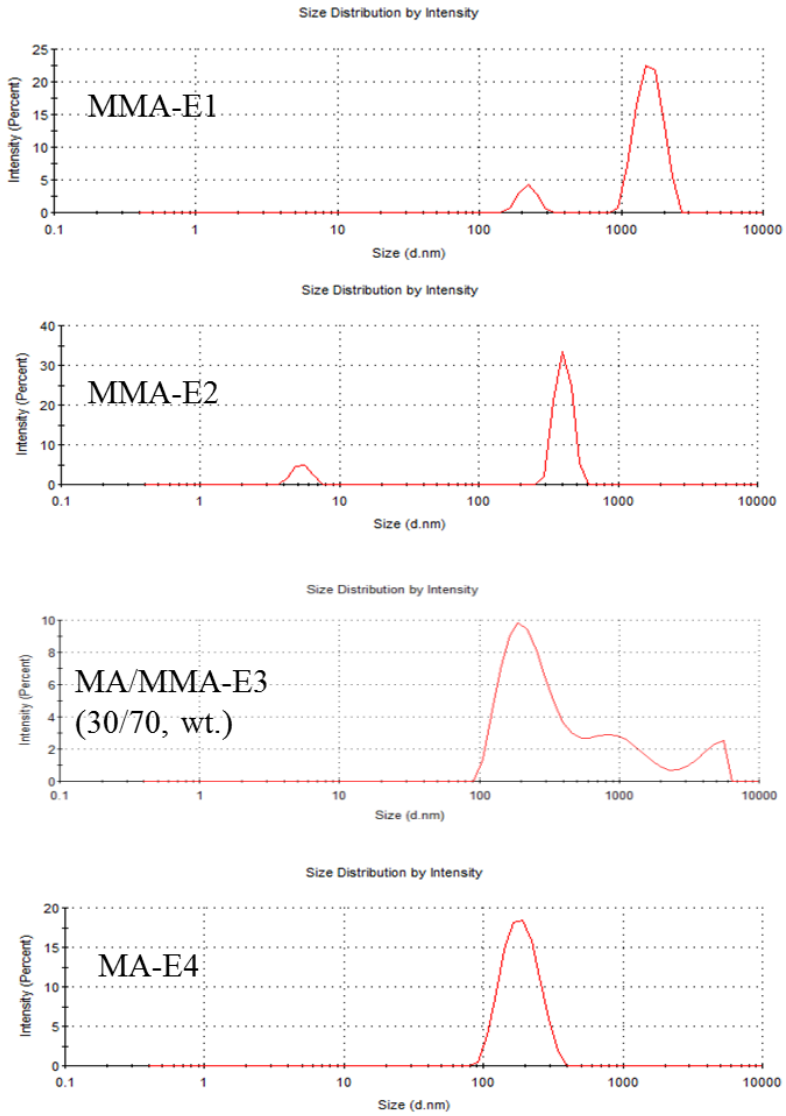

Figure 2. Particle size distributions measured by DLS for NAD dispersions: P(MMA) dispersion measured at 60 min using macromonomer (E1); P(MMA) dispersion measured at 60 min using non-reactive dispersant (E2); P(MA-co-MMA) final dispersion product using non-reactive dispersant (E3); and P(MA) final dispersion product using non-reactive dispersant (E4).

Hansen solubility parameters (HSP), often applied to estimate compatibility between solvent and polymer in industry, are used in this study to quantify the relative affinity between components of the system. A few studies have used HSPs to characterize batch dispersions of nonpolar monomers in polar solvent mixtures with varied monomer[20] and solvent compositions.[21,22] The semi-batch system is very different, as it involves a continuous phase that contains low monomer concentrations (starved-feed operation) in a non-polar solvent mixture. Yang and Hutchinson[18] first proposed the use of HSPs to interpret results for NADs produced with the same experimental procedure as used in this study. It was found that small changes in particle polarity introduced by varying copolymer composition (either by addition of less-polar styrene or more-polar functional monomers) did not correlate with the observed changes in particle size in the presence of P(BMA) macromonomer as the dispersant. This conclusion is contrary to what is found above using a non-reactive P(BMA) dispersant, for which larger variations in the core composition are highly correlated to system stability, particle size and particle size distribution.

The same paper[18] used HSP to explain why it was not possible to achieve a stable dispersion with 10 and 15 mol% HEMA added as a comonomer to P(BMA) macromonomer, due to a lowered affinity between the dispersant (which becomes more polar with the addition of HEMA) and the continuous phase. Two potential strategies for improving system stability are investigated in this study, increasing the polarity of the solvent mixture to match the increased polarity of the P(BMA-ran-HEMA) dispersant, and decreasing the polarity of the hydroxyl-containing macromonomer to increase the affinity between the dispersant and solvent.

Table 3 gives the HSP of all solvents, core composition and dispersants used in this study, with the overall Hansen solubility parameter, δ_T, calculated from the dispersion, polar, and hydrogen-bonding contributions (Equation (1)).[25]

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (1)$$

Equation (2)[25] is used to calculate Hansen solubility parameters of a mixture from the pure component values,

$$\delta_{mix} = (\varphi_{comp1} \times \delta_{comp1}) + (\varphi_{comp2} \times \delta_{comp2}) + (\varphi_{comp3} \times \delta_{comp3}) \quad (2)$$

with $\varphi_{com,i}$ and $\delta_{com,i}$ indicating volume fraction and specific Hansen solubility parameter of component-*i* in the mixture. As seen in Table 3, among the solvents investigated xylene has a larger value of δ_H, indicating increased H-bonding than heptane, but lower than that of butyl acetate. For particle core compositions, P(MMA) has a reduced δ_H and δ_T than P(MA), and the new macromonomer dispersant investigated, P(EHMA), has a smaller values of δ_H and δ_T than P(BMA), while P(HEMA) has the largest values due to the hydrogen-bonding it introduces. Equation (3) uses these values to calculate solubility distance R_a, a measure of the compatibility between different components 1 and 2,[25] with a smaller value indicating higher affinity between the components.

$$R_{a,12}^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2 \quad (3)$$

Solubility distances between ~~solvent~~ solution and dispersant ($R_{\frac{sol}{dis}}$), ~~solvent~~ solution and core polymer ($R_{\frac{sol}{cor}}$), and dispersant and core polymer ($R_{\frac{cor}{dis}}$) are calculated to characterize the impact of changing ~~solvent~~solution, dispersant, or core polymer composition in the NAD system. The solution values are calculated based upon the monomer-free solvent/dispersant mixture at the start of the semi-batch reaction. While the composition varies over the course of the reaction with feed addition and dispersant incorporation to the particle phase, the change is slight due to the starved-feed operating policy employed.[2]

Table 3. Hansen solubility parameters of components in the NAD systems studied.

Chemicals	$\boldsymbol{\delta_D}$ [a)]	$\boldsymbol{\delta_P}$ [a)]	$\boldsymbol{\delta_H}$ [a)]	$\boldsymbol{\delta_T}$ [d)]
Heptane	15.3	0	0	15.3
Xylenes[b)]	17.8	1	3.1	18.1
Butyl acetate	15.8	3.7	6.3	17.4
P(MA)	17.4	4.3	6.5	19.1
P(MMA)	16.2	1.6	4.7	16.9
P(HEMA)	17.1	5	12.1	21.5
P(BMA)	16.1	1.4	3.5	16.5
P(EHMA)[c)]	15.9	0.9	2.5	16.1

[a)] Data is from data store of HSPiP software (Version 5.0.05) with units $MPa^{1/2}$; [b)] xylene isomers have the same Hansen solubility parameters; [c)] Data is from group prediction method after correction (details in Supporting Information); [d)] δ_T is total solubility parameter with units $MPa^{1/2}$, consisting of three contributions δ_D (contribution of dispersion), δ_P (contribution of polar force) and δ_H (contribution of hydrogen bonding force), calculated by Equation (1).

3.2 Effect of Solvent

Heptane is the base hydrocarbon in the standard NAD experimental procedure, with xylenes also present as the solvent for the dispersant such that the initial w/w ratio of xylenes to heptane in the reactor is 0.4/1. As shown in Figure 3, the resulting δ_T of the system is 16.0 $MPa^{1/2}$, close to the value of the P(BMA) macromonomer dispersant (16.5), but significantly lower than the value for the more polar P(MA) particles formed (19.1). These values are used to calculate the solubility distances summarized in Table 4 for this base case (E5). Two experiments were run to explore the effect of increasing the HSP of the solvent mixture on NAD properties, one with butyl acetate replacing the heptane component (E7), and the second with a portion of the heptane charge replaced with xylenes to give an initial w/w ratio of 1.8/1 (E6). All other aspects of the experimental procedure, including total solvent fraction, were kept constant. Figure 3 summarizes the relative values of δ_T for the three solvent/dispersant solution mixtures compared to that of the P(BMA) dispersant and the P(MA) core polymers.

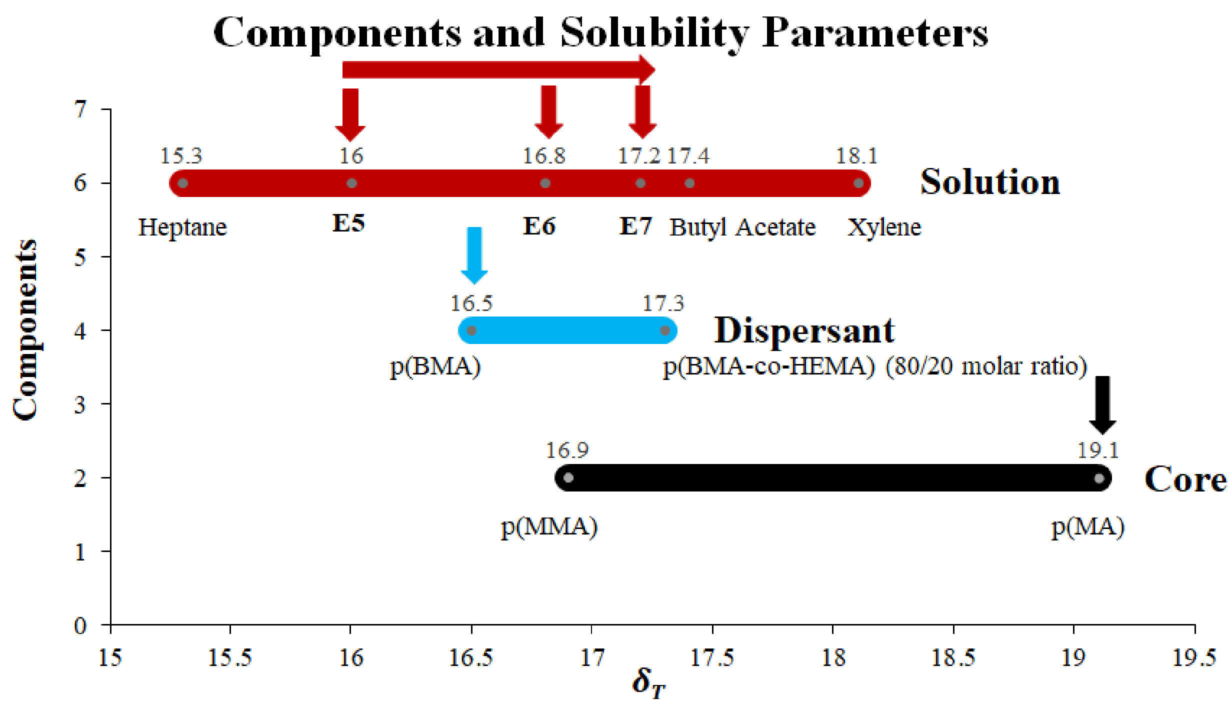

Figure 3. Component δ_T values ($MPa^{1/2}$) for P(MA) NADs produced with P(BMA) macromonomer dispersant with varying solvent compositions (as indicated).

Increasing the polarity of the solvent decreases the value of $R_{\frac{sol}{cor}}$ from 7.02 to 3.25 $MPa^{1/2}$. The effect of this change on the NAD system is quite significant, as summarized in Table 4: average particle size increases significantly and the PSD becomes bimodal. The decreased value of $R_{\frac{sol}{cor}}$ indicates increased compatibility between the core polymer and the ~~solvent~~ solution such that the dispersion polymerization shifts more towards ~~solution~~ homogeneous polymerization, as indicated by the lower M_n of the P(MA) particle core. The increased affinity between the particle and ~~solvent~~ continuous phase is also reflected in the quite significant increase in particle size observed.

Table 4. Solubility distances and corresponding properties of P(MA) NADs produced with P(BMA) macromonomer dispersant with varying solvent composition. (HSP values of solvent/dispersant mixtures in Supporting Information).

Exp. solvent mixture (w/w)[a)]	$\boldsymbol{R_{\frac{sol}{cor}}}$ [b)]	$\boldsymbol{R_{\frac{sol}{dis}}}$ [b)]	$\boldsymbol{R_{\frac{cor}{dis}}}$ [b)]	**Particle average size [nm] and PSD**	$\boldsymbol{M_n}$ [c)] **[Da]**	**Đ**	$\boldsymbol{W_{inc}}$	**Viscosity [cps]**
E5; 0.4/1.0 Xyl/Hept	7.02	2.34	4.92	95; Unimodal, PDI = 0.073	20300	4.3	0.74	270
E6; 1.8/1.0 Xyl/Hept	5.76	1.74	4.92	226; Multimodal, PDI = 0.715	13700	2.9	0.52	472
E7; 0.4/1.0 Xyl/BuAc	3.25	1.84	4.92	141; Multimodal, PDI = 0.677	13300	3.0	0.67	> 2,000

[a)] Solvent mass ratios; Xyl = xylenes, Hept = heptane, BuAc = butyl acetate; [b)] Solubility distances with unit $MPa^{1/2}$; [c)] Number average molecular weight of particle core after centrifugation of NAD, using PS calibration.

The observed trends are the same as Cockburn *et al.*[11] reported for dispersion polymerization of MMA with increasing methanol fraction in a methanol/water mixture using poly(N-vinyl pyrrolidone) as the dispersant; in that work the result was attributed to the influence of solvency on monomer partitioning and an increased fraction of reaction occurring in the continuous phase due to the increased solubility of the growing polymer radicals. In our system, the important contribution of the reactive macromonomer dispersant complicates the interpretation of the results, as seen in the data for incorporated fraction of macromonomer (W_{inc}). As summarized in Table 4, a smaller value of $R_{\frac{sol}{dis}}$, indicating increased compatibility of the dispersant and the solution~~vent~~, is correlated to a lowering of W_{inc}. This decrease also impacts M_n and reduces the dispersity (Đ) of the P(MA), as fewer dispersant molecules react with the chains that are incorporated into the particle core. As the value of $R_{\frac{sol}{dis}}$ influences the effectiveness of dispersant incorporation, it also affects the stability, particle size and PSD of the system. Another important finding, verified by additional experiments discussed later, is that increased affinity between the solution~~vent~~ and core ($R_{\frac{sol}{cor}} < 6$) favors multimodal particle distribution.

The choice of solvent mixture also greatly impacts the viscosity of the NAD system. Typically, the viscosity of particle dispersions increases with higher solids content, smaller particle size and narrower particle size distributions.[26] However, in this experimental set, solvent choice is a more important factor: E7 has much larger particles and a broader size distribution than E5, but also has a much higher viscosity (2000 vs. 270 cps). This result may be attributed to the increased hydrogen bonding with the more polar butyl acetate (Table 3, δ_H = 6.3 MPa$^{1/2}$). As the hydrogen bonding effect on viscosity is broadly reported for aqueous[27] but not for non-aqueous systems, its effect will be further tested in the following experiments.

3.3 Effect of HEMA Content in the P(BMA) Based Macromonomer Dispersant

Introducing HEMA as a comonomer to the dispersant is important for end-use application, as more than 30% of the low MW material is not incorporated onto the particles; the added hydroxyl groups ensure that these chains become cross-linked into the final coating rather than remain as extractable material. In this section, the performance of macromonomer containing 5 and 10 mol% HEMA content is compared to the P(BMA) homopolymer macromonomer, keeping the MWs of the materials almost identical (see Table 1). As illustrated in Figure 4, introducing HEMA to the dispersant increases the HSP of the material from its initial value of 16.5 to 16.9 MPa$^{1/2}$, further from the HSP of the solvent mixture and closer to the value for the particle core, with Table S4 summarizing the specific HSP data for the three different P(BMA) based macromonomers.

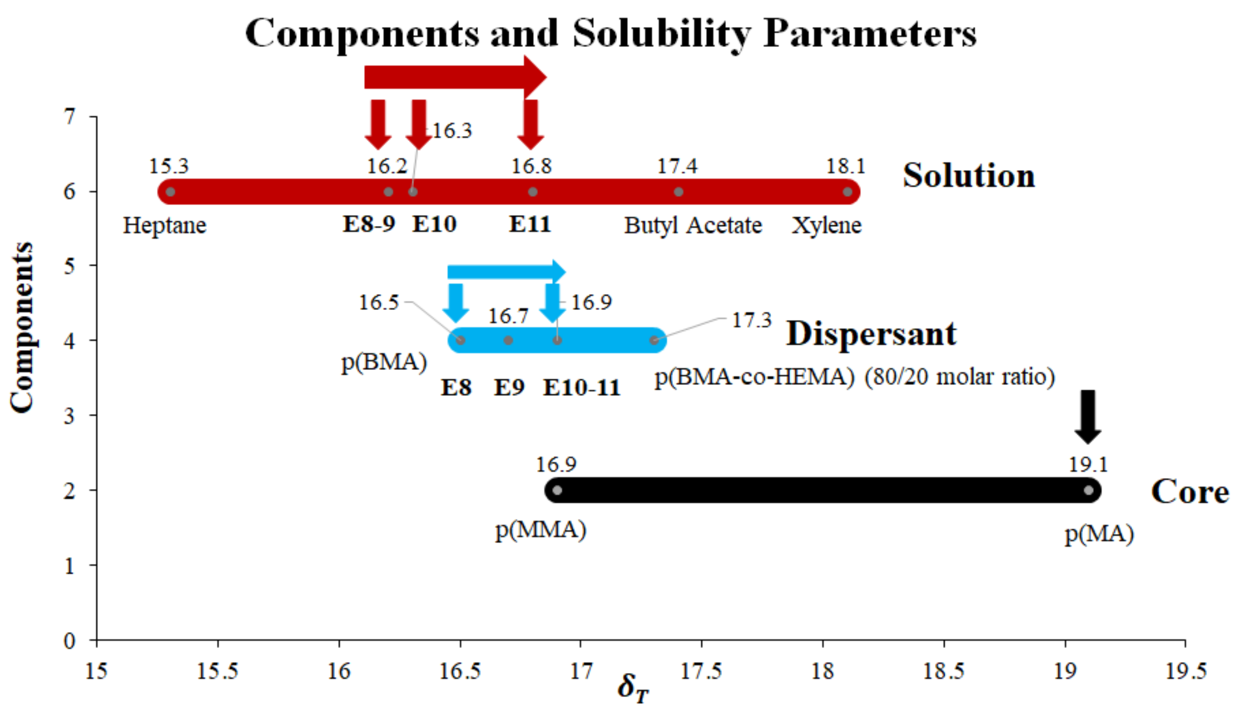

Figure 4. Varying δ_T values ($MPa^{1/2}$) of P(BMA) based macromonomer synthesized with different amount of HEMA as comonomer, relative to the values for P(MA) as the core and the standard heptane/xylene solvent mixture and E11 (simultaneous variation of the solvent and P(BMA) macromonomer composition).

In the previous study,[18] it was found that the P(BMA) macromonomer containing 10 mol% HEMA could not produce stable NAD under the standard feeding procedure (two-thirds of the dispersant added at the beginning of the batch and one-third fed with the MA monomer). Thus, in the current set of experiments, all of the P(BMA) based macromonomer was added to the reactor before feeding the MA. As solubility distances are calculated based on the initial mixture composition, this change in procedure slightly modifies the values of $R_{\frac{sol}{cor}}$ and $R_{\frac{sol}{dis}}$ for Experiment E8 compared to E5. Although this process modification somewhat improved the stability, there is still significant coagulation using the macromonomer containing 10 mol% HEMA (see Figure 5), as is similarly reported in Yang's thesis.[28] The detailed experimental results are summarized in Table 5 (E8-E10).

Table 5. Solubility distances and corresponding properties of P(MA) NADs produced with P(BMA) based macromonomers containing varying amounts of HEMA as comonomer. (HSP values in Supporting Information).

Exp. Dispersant Comp.[a)]	$R_{\frac{sol}{cor}}$ [b)]	$R_{\frac{sol}{dis}}$ [b)]	$R_{\frac{cor}{dis}}$ [b)]	Particle average size [nm] and PSD	M_n [c)]	Đ	W_{inc}	Vis. [cps]	Stability
E8 100/0	6.58	1.96	4.92	94; Unimodal, PDI = 0.073	18100	4.22	0.83	348	Stable
E9 95/5	6.46	2.30	4.50	98; Unimodal, PDI = 0.097	20600	4.52	0.89	506	Stable
E10[d)] 90/10	6.33	2.64	4.10	57; Unimodal, PDI=0.111	19000	5.15	-	-	Not stable
E11[e)] 90/10	5.54	2.29	4.10	171; Multimodal, PDI = 0.922	-	-	-	1121	Stable

[a)] Dispersant composition given as BMA/HEMA mole fraction; [b)] Solubility distances with unit MPa$^{1/2}$; [c)] Number average molecular weight of particle core after centrifugation of NAD, using PS standard calibration; [d)] Properties reported for sample collected at 110 min. [e)] Experiment conducted with xylene to heptane solvent mass ratio of 1.8 to 1.

All three experiments produced unimodal PSDs (see Supporting Information), despite the loss in system stability for experiment E10. This result is in contrast to those in Section 3.2, where the NAD system remained stable but the PSD became bimodal when $R_{\frac{sol}{cor}}$ was decreased to values lower than 6 MPa$^{1/2}$. Increasing the HEMA content in the dispersant from 0 to 5 mol% did not significantly influence the average particle size (95-100 nm); although the value of W_{inc} increased slightly, the M_n and Đ values of the core P(MA) polymer are similar. The latter values are also similar for the experiment conducted with P(BMA) dispersant containing 10 mol% HEMA, although the particles formed before the point of coagulation (110 min) are significantly smaller.

The value of $R_{\frac{sol}{dis}}$ increases with increasing HEMA content in the macromonomer, while the value of $R_{\frac{cor}{dis}}$ decreases. The latter change indicates an increased affinity of the dispersant with the particle, while the former shows a decreased affinity between dispersant and ~~solvent~~continuous phase. Both changes could affect the system stability by causing the dispersant to partition more to the particle, consistent with the observed increase in W_{inc} from E8 to E9. Because of the increased $R_{\frac{sol}{dis}}$, the dispersant chains will not be as effective in stabilizing the particles, as the polar HEMA groups on the molecules are more attracted to the surface (or interior) of the P(MA) core, not extending in the medium. Thus, despite the well-controlled particle size, some coagulation on the agitator is observed even with only 5 mol% HEMA in the dispersant molecules (Figure 5). There is more significant coagulation of the dispersion on the agitator for the P(BMA) macromonomer containing 10 mol% HEMA (E10), and the entire dispersion becomes unstable. In addition, the viscosity increases from 348 cps to 506 cps when 5 mol% HEMA is introduced to the dispersant, even though E9 has slightly larger average particle size (98 nm > 94 nm) and a broader particle size distribution (0.097 vs. 0.073 PDI). This increase can be explained by the hydrogen bonding forces introduced by the HEMA content in the dispersant.

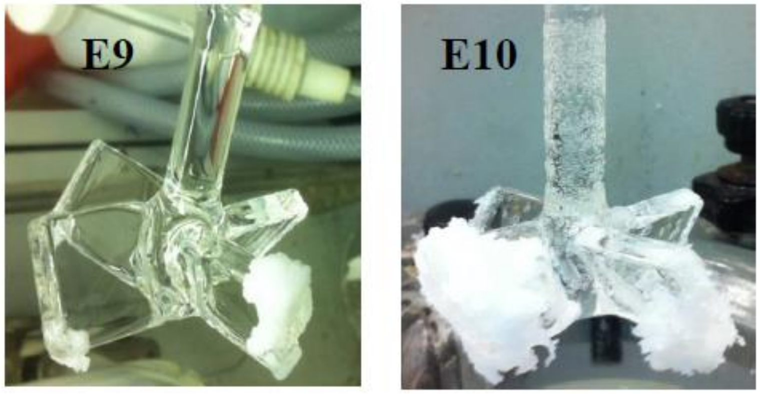

Figure 5. Coagulation observed in E9 and E10 conducted with HEMA-containing P(BMA) macromonomer. (See Table 5 for experimental details.)

3.4 Simultaneous Variation of the Solvent and P(BMA) Macromonomer Composition

The results presented in the previous sections suggest that a feasible means to achieve stability while adding HEMA content to the P(BMA) based macromonomer is to increase the HSP value of the ~~solvent mixture~~continuous phase to match the increasing dispersant value. As illustrated conceptually by Figure ~~6~~ 4, this strategy should keep $R_{\frac{sol}{dis}}$ small to promote compatibility between the ~~solvent~~ solution and dispersant and keep the dispersion stable. This hypothesis is tested with E11, which uses the same solvent mixture as E6 (i.e., with increased xylene content compared to the usual recipe) combined with the P(BMA) macromonomer containing 10 mol% HEMA. The result of this important experiment is summarized by the last entry in Table 5.

Adjusting the solvent composition to maintain $R_{\frac{sol}{dis}}$ at a value closer to 2 MPa$^{1/2}$ succesfully provided a stable final dispersion with the more polar copolymer dispersant; however, the corresponding decrease in $R_{\frac{sol}{cor}}$ to less than 6 MPa$^{1/2}$ resulted in a multimodal particle size distribution. In addition, simultaneously increasing the values of δ_T for the ~~solvent~~ solution and the dispersant led to a significant increase in viscosity of the system to >1000 cps, even though solids content remains constant and particle size increased. Thus, although the final dispersion produced with the HEMA-containing dispersant is stable, the properties of the NAD product (higher d_P and viscosity) are degraded.

3.5 NAD System with P(EHMA) Based Macromonomer

The above analysis demonstrates that there is a very limited operating window available to produce stable P(MA) dispersions employing a P(BMA-ran-HEMA) macromonomer dispersant. However, the insights gained from examining HSP and solubility distances suggests a means to design a new macromonomer dispersant, substituting the less-polar EHMA for BMA as the principal monomer. It was our hypothesis that the lowered δ_T value of P(EHMA) compared to P(BMA) (see Table 3) should result in increased compatibility between dispersant and solvent even with HEMA added as a comonomer to the dispersant. The calculated solubility distances between the different components are illustrated in Figure 6~~7~~ and summarized in Table 6 (E12-E15) for a series of P(EHMA-ran-HEMA) macromonomer dispersants containing up to 24 mol% HEMA.

Table 6 summarizes the properties of the NAD dispersions obtained with the P(EHMA) based macromonomer dispersants. As the value of $R_{\frac{sol}{cor}}$ has not changed significantly for the system (close to 7.0), it was expected that all final PSDs would remain unimodal, as found experimentally (Supporting Information). In addition, all experiments resulted in a final stable dispersion, even with 24 mol% HEMA in the EHMA-based dispersant (E15). This latter result is somewhat surprising, as the $R_{\frac{sol}{dis}}$ value of 3.30 is greater than that of the unstable NAD produced with P(BMA)-based dispersant with 10 mol% HEMA (2.64, E10). ~~However, the $R_{cor/dis}$ value for this P(EHMA)-based dispersant remains higher than the P(BMA)-based systems, indicating an increase in the stabilizing power per dispersant chain; *i.e.*, the dispersant that successfully attaches to the~~

~~core is able to well stabilize the particles due to its decreased solubility distance to the solvent compared to the core.~~

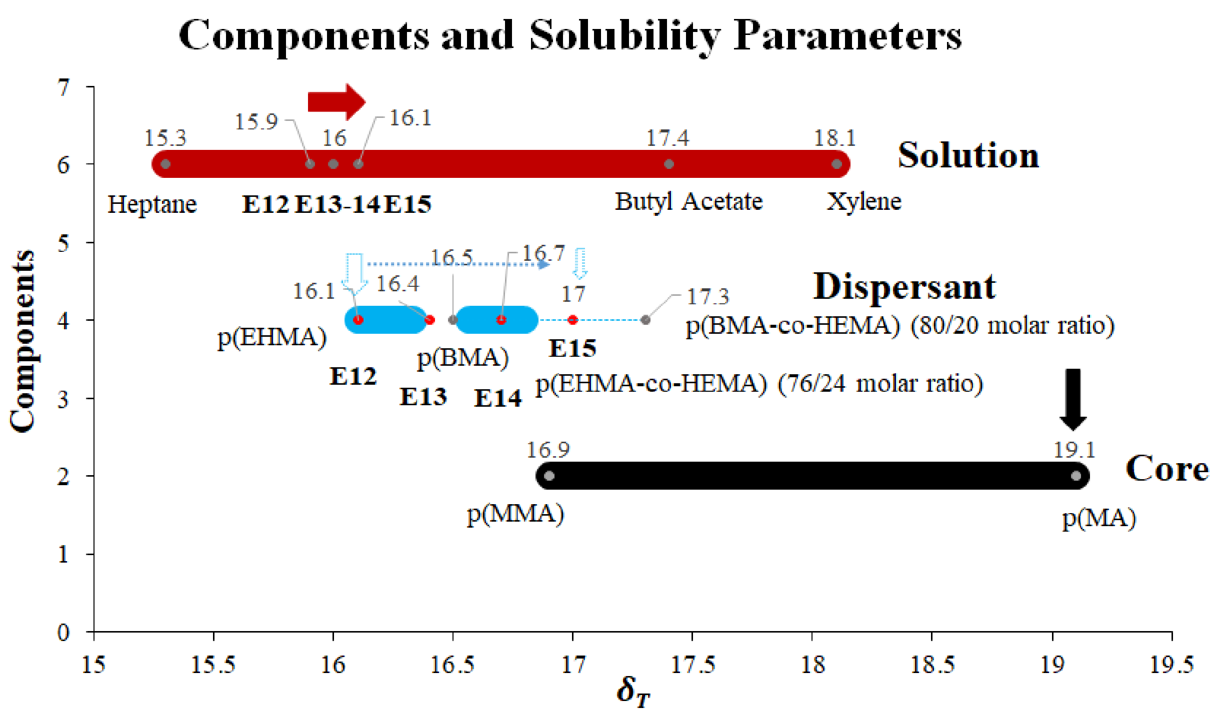

Figure 6. Design of P(EHMA-ran-HEMA) based macromonomers (red dots) with lower $\boldsymbol{\delta_T}$ values relative to the values for P(BMA-ran-HEMA) macromonomers (grey dots). Values shown are relative to the solution (continuous phase) and P(MA) homopolymer core.

The increased particle size produced with the P(EHMA) macromonomer (E12, d_P=115 nm) compared to the P(BMA) macromonomer (E8, d_P=94 nm) may be a result of the decreased dispersant incorporation that correlates with a decrease in the value of $R_{\frac{sol}{dis}}$. Compared with P(BMA) macromonomer, the P(EHMA) macromonomer tends to stay more in the medium with a lessened incorporation rate (smaller W_{inc}) but, as expected, P(EHMA) has better stabilization because the polymer chain is more compatible with the medium. As the HEMA content in the P(EHMA) macromonomer is increased, the offered stability per incorporated dispersant decreases only slightly, such that the particle size of the final NAD increases from 115 nm to 131 nm. As in the other experiment series, there is good correlation between Đ and W_{inc}, with Đ increasing with

W_{inc}. Note that (as further detailed in Supporting Information) the effective stabilization of the NAD particles by the P(EHMA) based dispersant made it impossible to fully separate them from the continuous phase.

Table 6. Solubility distances and properties for P(MA) NAD system using P(EHMA) based macromonomers with varying amounts of HEMA as comonomer. (HSP values in Supporting Information).

Exp. dispersant comp.[a]	$R_{\frac{sol}{cor}}$[b]	$R_{\frac{sol}{dis}}$[b]	$R_{\frac{cor}{dis}}$[b]	**Particle average size [nm] and PSD**	M_n[c] **[Da]**	**Đ**	W_{inc}[d]	**Vis. [cps]**
E12 100/0	7.24	1.41	6.05	115; Unimodal, PDI=0.058	12330	4.27	0.73	112
E13 92/8	7.04	2.03	5.27	115; Unimodal, PDI=0.088	14690	3.95	0.75	124
E14 84/16	6.83	2.67	4.52	120; Unimodal, PDI=0.073	17050	3.82	0.68	469
E15 76/24	6.62	3.30	3.82	141; Unimodal, PDI=0.097	16640	4.24	0.77	>2000

[a] Dispersant composition given as BMA/HEMA mole fraction; [b] Solubility distances with unit $MPa^{1/2}$; [c] Number average molecular weight of particle core after centrifugation of NAD, using PS standard calibration; [d] Upper phase liquid showed slight turbidity after separation from particles, such that true values of W_{inc} are lower (see Supporting Information).

Additional experiments were conducted with the P(EHMA) macromonomer in order to confirm that an increased xylene content in the solvent leads to higher viscosity. All other conditions were as for E12, with 20 and 80 wt% xylenes in the initial solvent charge, respectively, rather than 100% heptane. While the PSD remained unimodal, average particle size increased from 115 to 194 nm, and the viscosity of the NAD mixture increased from 112 to 590 cp with the increased xylene content, despite the larger average particle size and broader PSDs obtained in the experiments.

4. Conclusions

The physical interactions among particle core, dispersant and ~~solvent~~ continuous phase in a NAD dispersion have been quantified using Hansen solubility parameters and correlated to NAD particle size distribution, viscosity and dispersion stability. It is found that the value of $R_{\frac{sol}{cor}}$ relates to the particle size distribution; for the system studied here a value greater than 6.3 $MPa^{1/2}$ resulted in a unimodal partice size distribution in all cases. ~~The $R_{sol/dis}$ value is a measure of the stability per dispersant chain, with a lower value indicating better stability, while the $R_{cor/dis}$ value correlates to the partition of dispersant, with a higher value indicating lowered incorporation to the particle.~~ NAD viscosity is correlated with the hydrogen bonding force contributed by the hydroxyl group of the dispersant or by solvent, with higher δ_H values leading to increased viscosity.

By manipulation of the compatibility between the components, we successfully produced stable NAD dispersions with unimodal PSDs and low viscosities even using macromonomer dispersant containing greater than 10 mol% HEMA. This success was achieved by changing the core monomer of the dispersant from BMA to EHMA, a substitution that significantly increased the stability per dispersant chain (lowered $R_{\frac{sol}{dis}}$) with only a slight decrease in the fraction of dispersant incorporated to the core particle. The success points the way to further systematic design of dispersant recipes to match product requirements. In addition, the application of new macromonomers with uniform dispersity (Đ<1.4) are under investigation.

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Keywords: macromonomer; nanoparticles; thermodynamics; viscosity; Hansen solubility parameters

References

[1] R. Dowbenko, D. P. Hart, *Ind. Eng. Chem. Prod. Res. Dev.* **1973**, *12*, 14.

[2] W. Yang, R. A. Hutchinson, *Macromol. React. Eng*. **2016**, *10*, 71.

[3] S. Sugihara, A. Blanazs, S. P. Armes, A. J. Ryan, A. L. Lewis, *J. Am. Chem. Soc.* **2011**, *133*, 15707.

[4] S. Kobayashi, H. Uyama, S. W. Lee, Y. Matsumoto, *J. Polym. Sci. Pol. Chem.* **1993**, *31*, 3133.

[5] S. Kobayashi, H. Uyama, Y. Narita, *Makromol. Chem. Rapid. Commun.* **1992**, *13*, 337.

[6] S. Kawaguchi, M. A. Winnik, K. Ito, *Macromolecules* **1995**, *28*, 1159.

[7] S. Kiatkamjornwong, C. Kongsupapsiri, *Polym. Int.* **2000**, *49*, 1395.

[8] W. Yang, D. Yang, C. Wang, S. Fu, *J. Polym. Sci. Polym. Chem. Ed.* **2001**, *39*, 555.

[9] K. Ishizu, M. Yamashita, A. Ichimura, *Polymer* **1997**, *38*, 5471.

[10] K. Ishizu, N. Tahara, *Polymer* **1996**, *37*, 2853.

[11] R. A. Cockburn, T. F. L. McKenna, R. A. Hutchinson, *Macromol. React. Eng.* **2011**, *5*, 404.

[12] L. Houillot, C. Bui, C. Farcet, C. Moire, J. A. Raust, H. Pasch, M. Save, B. Charleux, *ACS Appl. Mater. Interfaces* **2010**, *2*, 434.

[13] L. Houillot, C. Bui, M. Save, B. Charleux, C. Farcet, C. Moire, J. A. Raust, I. Rodrigues, *Macromolecules* **2007**, *40*, 6500.

[14] L, Antl, J. W.Goodwin, R. D. Hill, R. H. Ottewill, S. M. Owens, S. Papworth, J. A. Waters, *Colloids Surf*. **1986**, *17*, 67.

[15] R. H. Pelton, A. Osterroth, M. A. Brook, *J. Colloid Interface Sci.* **1990**, *137*, 120.

[16] M. D. Croucher, T. H. Milkie, *Faraday Discuss. Chem. Soc.* **1983**, *76*, 261.

[17] R. J. Barsotti, L. A. Lewin, C. Scopazzi, *U.S. Patent* 5,763,528, **1998**.

[18] W. Yang, R. A. Hutchinson, *React. Funct. Polym*. **2017**, *114*, 31.

[19] A. N. Nikitin, M. C. Grady, G. A. Kalfas, R. A. Hutchinson, *Macromol. React. Eng*. **2008**, *2*, 422.

[20] A. C. Simmons, *Opt. Commun.* **1978**, *25*, 211.

[21] L. Grunberg, A. H. Nissan, *Nature* **1949**, *164*, 799.

[22] Y. Saadat, S. Hosseinzadeh, F. Afshar-Taromi, H. Eslami, S. Abdolbaghi, *Colloids Polym. Sci.* **2013**, *291*, 937.

[23] D. Horák, F. Švec, J. M. J. Fréchet, *J. Polym. Sci. Part A Polym. Chem.* **1995**, *33*, 2329.

[24] K. P. Lok, C. K. Ober, *Can. J. Chem.* **1985**, *63*, 209.

[25] C. M. Hansen, *Hansen Solubility Parameters A User's Handbook*, 2nd ed., Taylor & Francis Group, **2007.**

[26] V. Y. Rudyak, S. L. Krasnolutskii, *Physics Letters A* **2014**, *378*, 1845

[27] B. Bris, P. Luckham, S. Zhu, *Polymer* **2000**, *41*, 3851.

[28] W. Yang, *Ph.D. Thesis*, Queen's University (Kingston Canada), **2016.**

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Design of acrylic dispersants for non-aqueous dispersion polymerization: the importance of thermodynamics

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Quantification of relative compatibilities between solution, dispersant and particles leads to the design of a new reactive macromonomer dispersant that provides increased particle stability in a high-solids non-aqueous dispersion system.