

# Particle formation in RAFT-mediated Emulsion Polymerization

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# Declaration of Originality

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“Croyez ceux qui cherchent la vérité, doutez de ceux qui la trouvent.” André Gide

# Table of Contents

<b>Summary</b>	<b>iii</b>
<b>Glossary</b>	<b>v</b>
Acronyms	v
Symbols	v
<b>Chapter 1 Introduction</b>	<b>1</b>
1.1 Colloidal stability of aqueous polymer dispersions	1
1.2 Emulsion Polymerization	2
1.3 Controlled radical polymerization	2
1.4 Controlled radical polymerization in heterogeneous media	4
1.5 Amphipathic macro-RAFT agents in emulsion	5
1.6 Scope of this thesis	6
1.7 References	7
<b>Chapter 2 Calorimetric study of particle formation</b>	<b>9</b>
2.1 Introduction	10
2.1.1 Heat of polymerization	10
2.1.2 Kinetics of Emulsion Polymerization	11
2.1.3 Reaction calorimetry	11
2.1.4 Objectives	13
2.2 Experimental	13
2.2.1 Chemicals	13
2.2.2 Synthesis of hydrophilic macro-RAFT agent	14
2.2.3 Synthesis of amphipathic macro-RAFT agent	15
2.2.4 Controlled feed RC-1 experiments	15
2.3 Results & Discussion	17
2.3.1 Synthesis of macro-RAFT agents	17
2.3.2 Calorimetric reactions	19
2.3.3 Macro-RAFT agents compared	21
2.3.4 Use of more hydrophobic macro-RAFT agents	23
2.3.5 Sensitivity of RC-1e	24
2.4 Conclusions	24
2.5 References	25
<b>Chapter 3 Particle formation mechanism</b>	<b>27</b>
3.1 Introduction	28
3.2 Conventional emulsion polymerization	28
3.3 Nucleation in amphipathic RAFT systems	31
3.3.1 Derivation of a particle number expression from the mechanism	32
3.3.2 Sample implementation	35
3.4 Conclusions	36
3.5 References	37

<b>Chapter 4 Characterization of macro-RAFT agents</b>	<b>39</b>
4.1 Introduction	40
4.2 Experimental	44
4.2.1 Capillary Zone Electrophoresis	44
4.2.2 Liquid Chromatography	44
4.2.3 Mass spectrometry	45
4.3 Results & Discussion	46
4.3.1 Mass spectra of the initial macro-RAFT agents	46
4.3.2 Quantification of the initial macro-RAFT agents	49
4.3.3 Time evolution of the molecular weight distribution	53
4.3.4 Determination of particle formation time	56
4.4 Conclusions	58
4.5 References	59
<b>Chapter 5 Physical properties of the solution and latex</b>	<b>61</b>
5.1 Introduction	62
5.1.1 Surface tension	62
5.1.2 Maron titration	63
5.1.3 Determination of particle size distribution	64
5.2 Experimental	67
5.2.1 Characterization of colloidal particles	67
5.2.2 Surface Tension measurements	68
5.2.3 Maron titrations	68
5.3 Results & Discussion	69
5.3.1 Concentration of surface active species	69
5.3.2 Particle sizes	70
5.3.3 Surface area per macro-RAFT agent	79
5.4 Conclusions	82
5.5 References	83
<b>Chapter 6 Nucleation mechanism revisited</b>	<b>85</b>
6.1 Introduction	86
6.1.1 Mechanistic results	86
6.2 Comparison of modelling and experimental results	87
6.2.1 Defining the operating window	89
6.2.2 Surface covered by the macro-RAFT agents	90
6.2.3 Monomer concentration in the latex particles	92
6.2.4 Average number of radicals per particle	95
6.2.5 Sensitivity analysis model parameters	97
6.2.6 Number of RAFT agents per particle	99
6.3 Suggestions for future work	102
6.4 Conclusions	103
6.5 References	103
<b>Appendices:</b>	<b>106</b>
Appendix I: Supporting reaction curves	106
Appendix II: Separation of BA macro-RAFT agents under critical conditions	108
Appendix III: TEM particle size distributions with ImageJ	110
<b>Acknowledgements / Dankwoord</b>	<b>113</b>
<b>Curriculum Vitae</b>	<b>115</b>

# Summary

Particle formation in RAFT-mediated emulsion polymerization has been studied using reaction calorimetry. By measuring the heat flow during controlled feed *ab-initio* emulsion polymerization in the presence of amphipathic RAFT agents, particle formation by self-assembly of these species could be observed. Two different monomer systems, i.e. styrene and n-butyl acrylate, and various degrees of hydrophobicity of the initial macro-RAFT agents have been studied and compared.

The different macro-RAFT agents were synthesized by first forming a hydrophilic block of poly(acrylic acid) that would later on act as the electrosteric stabilizing group for the particles. Subsequently, different lengths of hydrophobic blocks were grown at the reactive end of the poly(acrylic acid) hydrophilic block via the RAFT-mediated controlled radical polymerization, either comprised of n-butyl acrylate or styrene.

Two processes govern particle formation: adsorption of macro-RAFT agents onto growing particles and formation of new particles by initiation of micellar aggregates or by homogeneous nucleation. Competition between these processes could be observed when monomers with a relatively high (n-butyl acrylate) or low (styrene) propagation rate coefficient were used.

A model describing particle formation has been developed and the results of model calculations are compared with experimental observations. Preliminary modeling results based on a set of reasonable physico-chemical parameters already showed good agreement with the experimental results. Most parameters used have been verified experimentally.

The development of the molecular weight distribution of the macro-RAFT agents has been analyzed by different techniques. Quantification of the particle formation process by analytical techniques was difficult, but qualitative insights into the fundamental steps

governing the nucleation process have been obtained. The amount of macro-RAFT agents initially involved in particle formation could be determined from the increase of molecular weight. The particle size distribution has been measured by capillary hydrodynamic fractionation, transmission electron microscopy and dynamic light scattering. From the data obtained from these particle-sizing techniques, the number of particles during the reaction could be monitored, leading to an accurate estimate for the particle formation time.

Upon implementation of the experimental data obtained for the surface active macro-RAFT systems, the model demonstrated to be very sensitive towards the “headgroup” area of the macro-RAFT species. Three nucleation cases based on the initial surface activity of the macro-RAFT species in the aqueous phase are proposed to explain the deviations from the assumptions of the nucleation model. Even though the macro-RAFT species have a narrow molecular weight distribution, they are nevertheless made up of a distribution of block lengths of polystyrene upon a distribution of block lengths of poly(acrylic acid). The resulting differences in initial surface activity are the most probable reason for the observed differences between model calculations and experimental results for the nucleation time and particle size distribution of the final latex product.

With the procedure described above, latexes have been synthesized without using conventional surfactants and the mechanisms involved in the particle formation for these systems have been elucidated. The results of this work enable production of latex systems with well defined molecular mass distributions and narrow particle size distributions. Furthermore, the technique based on the application of amphiphatic RAFT agents is promising for the production of complex polymeric materials in emulsion polymerization on a technical scale.

# Glossary

## Acronyms

AA	Acrylic acid
BA	Butyl acrylate
C(Z)E	Capillary (Zone) Electrophoresis
CHDF	Capillary Hydrodynamic Fractionation
CMC	Critical micelle concentration
DLS	Dynamic light scattering
DLVO	Theory of stability of lyophobic dispersions as developed by Derjaguin and Landau and independently by Verwey and Overbeek
DP	Degree of polymerization
DRI	Differential refractive index
Dx	Dioxane
EOF	Electro-osmotic flow
ESI-MS	Electrospray ionization mass-spectrometry
HDC	Hydrodynamic chromatography
HPLC	High performance liquid chromatography
HQ	Hydroquinone
HUFT	Homogeneous nucleation model described by Hansen and Ugelstad as well as by Fitch and Tsai
LAC	Liquid adsorption chromatography
MALDI-ToF MS	Matrix-assisted laser desorption ionization time-of-flight mass-spectrometry
MeHQ	Hydroquinone monomethyl ether
MWD	Molecular weight distribution
PDI	Polydispersity index
PFG	Column material for use with fluorinated solvents
PG	Propylene glycol
PLP-SEC	Pulsed laser polymerization in combination with SEC
PMMA	Poly(methyl methacrylate)
PSD	Particle size distribution
PVA	Poly(vinyl alcohol)
RAFT	Reversible addition-fragmentation chain transfer
SANS	Small angle neutron scattering
SDS	Sodium dodecyl sulfate
SEC	Size exclusion chromatography
STY	Styrene
(cryo-)TEM	(cryogenic) Transmission electron microscopy
THF	Tetrahydrofuran
UV	Ultra-violet
V-501	4,4'-Azobis(4-cyanopentanoicacid) also known as 4,4'-Azobis(4-cyanovalericacid)

## Symbols

symbol	definition	Typical units
$\Gamma$	Interfacial tension at the latex particle water surface	$10^{-3} \text{ N s}^{-1}$
$\rho$	Average number of radicals entering a particle	$\text{s}^{-1}$
$\rho_L$	Density of the latex particles	$\text{g L}^{-1}$
$\rho_M$	Density of monomer	$\text{kg m}^{-3}$
$\rho_P$	Density of polymer	$\text{kg m}^{-3}$



<b>symbol</b>	<b>definition</b>	<b>Typical units</b>
$\phi_p$	Volume fraction of polymer in the polymer solution constituting the latex particles	
$\chi$	Flory-Huggins interaction parameter	
$A$	Heat exchange area	$m^2$
$A_E$	Specific surface area of surfactant	$m^2$
$A_S$	Area of a particle	$m^2$
$A_{SDS}$	Total surface covered by SDS	$m^2 g^{-1}$
$C$	Total concentration of added surfactant	$mol L^{-1}$
$d_n$	Number average diameter	$10^{-9} m$
$d_{vv}$	Volume weighted average diameter	$10^{-9} m$
$d_z$	Intensity weighted average diameter	$10^{-9} m$
$[I]$	Initiator concentration	$mol L^{-1}$
$k$	Exit rate of radicals from a particle	$s^{-1}$
$K_d$	Initiator dissociation rate coefficient	$s^{-1}$
$K_p$	Propagation rate coefficient	$L mol^{-1} s^{-1}$
$K_{p,W}$	Propagation rate coefficient in the water phase	$L mol^{-1} s^{-1}$
$K_t$	Termination rate coefficient	$L mol^{-1} s^{-1}$
$K_{t,W}$	Termination rate coefficient in the water phase	$L mol^{-1} s^{-1}$
$m$	Concentration of polymer	$g L^{-1}$
$M_0$	Molecular weight of monomer	$kg mol^{-1}$
$m_{M^0}$	Mass of monomer per total volume	$g L^{-1}$
$[M]_p$	[Monomer] in the particles	$mol L^{-1}$
$[M]_w$	[Monomer] in the water phase	$mol L^{-1}$
$\bar{n}$	Time <number> of free radicals per particle	
$N_A$	Avogadro's number	$mol^{-1}$
$N_c$	Number concentration of particles	$L^{-1}$
$n_{cap}$	Number of RAFT capped chains per particle	
$n_{M^0}$	Moles of monomer per unit volume of water	$mol L^{-1}$
$n_{macro-RAFT}$	Number of macro-RAFT molecules	
$N_p$	Number of particles	
$Q_c$	Calibration heat	$W$
$r_u$	Average radius of the unswollen particles	$10^{-9} m$
$S_a$	Titrated soap adsorbed on the latex particles	$mol g^{-1}$
$T_a$	Corrected jacket temperature	$^{\circ}C$
$T_g$	Glass transition temperature	$^{\circ}C$
$T_j$	Temperature of the surrounding jacket oil	$^{\circ}C$
$T_r$	Temperature of the reaction mixture	$^{\circ}C$
$U$	Overall heat transfer coefficient	$W m^{-2}K^{-1}$
$V_s$	Monomer swollen volume	$m^3$
$V_{sM}$	Partial molar volume of monomer	$m^3$
$V_w$	Volume of water	$L$
$X_{crit}$	Critical degree of polymerization	
$\bar{X}_n$	Number-average degree of polymerization of chains	
$z$	Degree of polymerization necessary for a initiator derived radical to become surface active enough to enter a particle	