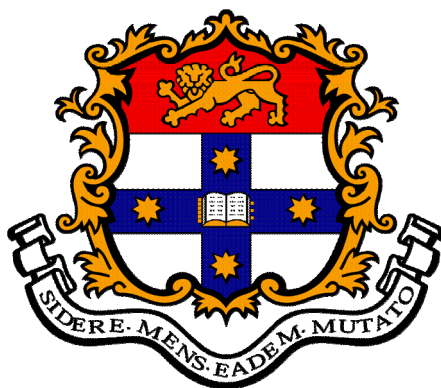# Particle formation in RAFT-mediated

Emulsion Polymerization

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Thesis submitted in fulfillment of the requirements

for the degree of Doctor of Philosophy

at the University of Sydney

July 2007

Declaration of Originality

I hereby declare that this submission is my own work and to the best of my knowledge it contains no materials previously published or written by another person, except where due acknowledgement is given. This thesis contains no material that has been presented for a degree or diploma at this or any other institute of higher education other than the author's submission at the Eindhoven University of Technology and the University of Sydney under the agreed cotutelle arrangement.

I also declare that the intellectual content of this thesis is the product of my own work, except to the extent that assistance from others in the project's design and conception or in style, presentation and linguistic expression is acknowledged.

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

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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 amphipathic 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 Ugelstadt 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
Γ	Interfacial tension at the latex particle water surface	10^{-3} N s^{-1}
ρ	Average number of radicals entering a particle	s^{-1}
ρ_L	Density of the latex particles	g L^{-1}
ρ_M	Density of monomer	kg m^{-3}
ρ_P	Density of polymer	kg m^{-3}

symbol	definition	Typical units
φ_p	Volume fraction of polymer in the polymer solution constituting the latex particles	
χ	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	$mol \, L^{-1}$
$n_{macro\text{-}RAFT}$	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	$°C$
T_g	Glass transition temperature	$°C$
T_j	Temperature of the surrounding jacket oil	$°C$
T_r	Temperature of the reaction mixture	$°C$
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	