

The Kinetics of Electrosterically Stabilized Emulsion Polymerization Systems



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“Gatsby believed in the green light; the orgiastic future that year by year recedes before us. It eluded us then, but no matter – tomorrow we will run faster, stretch our arms out farther, and one fine morning...

So we beat on, boats against the current, borne back ceaselessly into the past.”

F. Scott Fitzgerald, *The Great Gatsby*

Declaration of Originality

The work presented in this thesis was wholly carried out by me throughout the duration of my degree at The University of Sydney from 2004 to 2007. Experimental assistance with respect to use of some equipment was provided by various staff members and fellow researchers, however all data analysis and interpretation is my own. Transmission Electron Microscopy (TEM) image acquisition of my samples was performed by Dr Binh Pham and Dr Desi Ganeva. Electrospray-Ionization Mass Spectrometry sample analysis was performed by Ms Hollie Zondanos. Nuclear magnetic resonance analysis was performed by Dr Marianne Gaborieau at The University of Queensland. Their help is gratefully acknowledged.

Stuart Thickett

Glossary of Symbols and Abbreviations

α	'Fate parameter' of an exited monomeric radical
A	Collection of constants in conversion-time expression (s^{-1})
a	Intercept of linear-fit to steady-state polymerization period
AA	Acrylic acid
[AA]	Local concentration of acrylic acid units within the hairy layer
AIBN	Azobisisobutyronitrile
ANSTO	Australian Nuclear Science and Technology Organization
A_{part}	Surface area of a latex particle (nm^2)
a_s	Area per surfactant molecule at maximum packing density (nm^2)
ATRP	Atom Transfer Radical Polymerization
b	Slope of linear fit to steady-state polymerization period
c	Pseudo-first-order termination rate coefficient (s^{-1})
c^{**}	Concentration above which polymer chains are entangled
CF	Contraction factor
CHDF	Capillary hydrodynamic fractionation
CMC	Critical micelle concentration (M)
C_p	Monomer concentration within the particle interior (M)
C_p^{sat}	Saturated monomer concentration within the particle interior (M)

C_{tr}	Chain transfer constant
C_w	Monomer concentration within the aqueous phase (M)
C_w^{sat}	Saturated monomer concentration within the aqueous phase (M)
δ	Width of the hairy layer (nm)
δ	NMR chemical shift
Da	Dalton (unit of molecular weight)
D_h	Diffusion coefficient within the hairy layer ($m^2 s^{-1}$)
D_i	Diffusion coefficient of a polymeric chain of degree of polymerization i
DLS	Dynamic light scattering
DLVO	Derjaguin, Landau, Verwey and Overbeek theory
d_M	Density of monomer ($g L^{-1}$)
D_{mon}	Diffusion coefficient of a monomeric radical ($m^2 s^{-1}$)
DP	Degree of polymerization
d_p	Density of polymer ($g L^{-1}$)
D_p	Diffusion coefficient of a monomeric radical within particle interior ($m^2 s^{-1}$)
D_w	Diffusion coefficient of a monomeric radical in aqueous phase ($m^2 s^{-1}$)
E^\cdot	Exited radical
ESI-MS	Electrospray Ionization Mass Spectrometry
ESR	Electron Spin Resonance

f	Initiator efficiency
f_{entry}	Radical entry efficiency
ΔG^{hyd}	Change in Gibbs free energy of hydration (kJ mol^{-1})
GPC	Gel Permeation Chromatography
HDC	Hydrodynamic Chromatography
HEMA	Hydroxyethyl methacrylate
HPPS	High Performance Particle Sizing
HUFT	Hansen, Ugelstad, Fitch and Tsai Theory
IM_i^\bullet	Initiator-derived oligomer of degree of polymerization i
$[\text{I}]$	Initiator concentration (M)
j_{crit}	Critical degree of polymerization where a radical becomes water-insoluble
k	Exit rate coefficient (s^{-1})
k_{abs}	Rate coefficient of hydrogen-atom abstraction ($\text{M}^{-1} \text{s}^{-1}$)
k_{ads}	Diffusion controlled adsorption rate coefficient ($\text{M}^{-1} \text{s}^{-1}$)
k_{beta}	Rate coefficient of beta-scission (s^{-1})
k_{cr}	Exit rate coefficient with complete re-entry (s^{-1})
k_{ct}	Exit rate coefficient with complete aqueous-phase termination (s^{-1})
k_{d}	Rate coefficient for initiator decomposition (s^{-1})
k_{dM}	Rate coefficient for desorption of a monomeric radical from a particle (s^{-1})

k_e	Bimolecular entry rate coefficient ($M^{-1} s^{-1}$)
k_e^i	Bimolecular entry rate coefficient for an oligomer of length i ($M^{-1} s^{-1}$)
k_{entry}	Entry rate coefficient with possibility of desorption considered ($M^{-1} s^{-1}$)
k_p	Propagation rate coefficient ($M^{-1} s^{-1}$)
k_p^1	Propagation rate coefficient of a monomeric radical ($M^{-1} s^{-1}$)
k_{pi}	Propagation rate coefficient of an initiator fragment ($M^{-1} s^{-1}$)
KPS	Potassium persulfate
k_{pw}	Propagation rate coefficient in the aqueous phase ($M^{-1} s^{-1}$)
k_{re}	Rate coefficient of re-entry (bimolecular) ($M^{-1} s^{-1}$)
k_t	Bimolecular termination rate coefficient ($M^{-1} s^{-1}$)
$\langle k_t \rangle$	Average bimolecular termination rate coefficient ($M^{-1} s^{-1}$)
k_{tc}	Rate coefficient for termination by combination ($M^{-1} s^{-1}$)
k_{td}	Rate coefficient for termination by disproportionation ($M^{-1} s^{-1}$)
$k_t^{i,j}$	Rate coefficient for termination between an i -mer and j -mer ($M^{-1} s^{-1}$)
k_{tr}	Transfer rate coefficient ($M^{-1} s^{-1}$)
$k_{tr,pol}$	Rate coefficient for chain transfer to polymer ($M^{-1} s^{-1}$)
k_{trAA}	Rate coefficient for chain transfer to poly(acrylic acid) ($M^{-1} s^{-1}$)
k_{tw}	Rate coefficient for termination in the aqueous phase ($M^{-1} s^{-1}$)
M	Monomer unit
[M]	Concentration of monomer (M)

M_0	Molecular weight of monomer (g mol^{-1})
MAA	Methacrylic acid
MALDI-TOF	Matrix-assisted Laser Desorption Ionization Time-of-Flight
MCR	Mid-chain radical
MEHQ	Methyl ethyl hydroquinone
MMA	Methyl methacrylate
\bar{M}_n	Number-average molecular weight (g mol^{-1})
m_M^{excess}	Mass of excess monomer (g)
m_M^p	Mass of monomer in the particle phase (g)
m_p^0	Mass of polymer per unit volume (g L^{-1})
m_p^{seed}	Mass of seed polymer in the particle phase (g)
MW	Molecular weight
MWD	Molecular weight distribution
N_0	Number of particles containing no radicals
N_1	Number of particles containing one radical
N_1^m	Number of particles containing one monomeric radical
N_1^p	Number of particles containing one polymeric radical
N_A	Avogadro's Number
\bar{n}	Average number of radicals per particle

\bar{n}_0	Average number of radicals per particle at time $t = 0$
\bar{n}_{ss}	Steady-state average number of radicals per particle
n -BA	n -butyl acrylate
n_{chains}	Number of RAFT-capped chains per particle
n_M^0	Initial number of moles of monomer in seeded experiment (mol)
NMR	Nuclear Magnetic Resonance
N_n	Number of particles containing n radicals
N_{new}	Number of new particles formed (L^{-1})
N_p	Latex particle number (L^{-1})
N_{seed}	Seed particle number (L^{-1})
Φ_{HL}	Volume fraction of the aqueous phase within the hairy layer
$P(M)$	Number distribution of chains of molecular weight M
PCS	Photon Correlation Spectroscopy
P_{des}	Probability of successful desorption from a particle
PDI	Polydispersity index
P_e	Probability of true entry
PEG	Poly(ethylene glycol)
PEO	Poly(ethylene oxide)
PFG	Pulsed Field Gradient

PLP	Pulsed Laser Polymerization
polyAA	Poly(acrylic acid)
ppm	Parts per million
PSD	Particle size distribution
ρ	First-order entry rate coefficient (s^{-1})
ρ_{init}	Contribution of entry rate coefficient from chemical initiator (s^{-1})
ρ_{re}	First-order rate coefficient of re-entry (s^{-1})
ρ_{spont}	Spontaneous first-order entry rate coefficient (s^{-1})
ρ_{total}	Total first-order entry rate coefficient (s^{-1})
R	Universal gas constant ($J K^{-1} mol^{-1}$)
[R]	Radical concentration (M)
RAFT	Reversible Addition Fragmentation Chain Transfer
r_s	Swollen particle radius (nm)
r_u	Unswollen particle radius (nm)
S_a	Particle surface area per surfactant molecule (nm^2)
SANS	Small-angle neutron scattering
SDBS	Sodium dodecylbenzenesulfonate
SDS	Sodium dodecyl sulfate
SEC	Size Exclusion Chromatography

$[T^{\cdot}]$	Total radical concentration
T	Temperature (K)
TBHP	<i>tert</i> -butylhydroperoxide
TEM	Transmission Electron Microscopy
THF	Tetrahydrofuran
UV	Ultra-violet
V-50	2,2'-Azobis(2-methylpropionamidine)dihydrochloride
V-501	4,4'-azobis(4-cyanovaleric acid)
VA-086	2,2'-Azobis[2-methyl-N-(2-hydroxyethyl)propionamide]
V_s	Swollen volume of latex particle (nm ³)
V_w	Volume of water in the emulsion (L)
$w(\log M)$	SEC distribution as a function of the logarithm of molecular weight
w_p	Weight fraction of polymer
x	Fractional conversion
x_0	Fractional conversion at time $t = 0$
\bar{X}_n	Number-average degree of polymerization
z	Critical degree of polymerization where surface activity is attained

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Abstract

The kinetics of electrosterically stabilized emulsion systems was studied. The aim of this was to understand the impact that steric and electrosteric stabilizers have on the kinetics of particle growth and particle formation in the area of emulsion polymerization. The well-established mechanisms that govern these processes for emulsions stabilized by conventional low molecular weight surfactants were used as a reference point for comparative purposes.

Model latexes were synthesized that comprised of a poly(styrene) core stabilized by a corona of poly(acrylic acid). The advent of successful controlled radical polymerization techniques in heterogeneous media (via RAFT polymerization) allowed for latexes to be synthesized under molecular weight control. For the first time, the degree of polymerization of the stabilizing block on the particle surface was able to be controlled and verified experimentally using mass spectrometry techniques. Three latexes were made with different average degrees of polymerization of the stabilizing block; five, ten and twenty monomer units respectively.

A methodology was developed to remove the RAFT functionality from the polymer chains present in the emulsion while retaining the desired particle morphology. Oxidation with *tert*-butylhydroperoxide (TBHP) was proven to be successful at eliminating the living character provided by the thiocarbonyl end-group. Extensive dialysis and cleaning of the latex was performed to ensure no residual TBHP or reaction by-products remained. Latexes with poly(styrene) cores were chosen for this work as poly(*n*-butyl acrylate) latexes were shown to be influenced by chain transfer to polymer, providing an additional kinetic complication.

The three electrosterically stabilized emulsions were used as seed latexes in carefully designed kinetic experiments to measure the rate of polymerization as a function of time. Two independent techniques (chemically initiated dilatometry and γ -relaxation dilatometry) were used to measure the rate coefficients of radical entry (ρ) and exit (k) in these systems – the two

parameters that essentially govern the rate of particle growth. The latexes were chosen such that they satisfied ‘zero-one’ conditions (i.e. that any given latex particle contains at most one growing radical at any given time) in order to simplify data analysis. Three different chemical initiators were used, each yielding a radical with a different electric charge.

Results from γ -relaxation experiments demonstrated that the three electrosterically stabilized latexes gave very long relaxation times when removed from the radiation source, ultimately yielding very small k values. These values were up to a factor of 10 smaller than that predicted by the ‘transfer-diffusion’ model for exit for particles of that size. This reduction was attributed to a ‘restricted diffusion’ effect, where the exiting monomeric radical has to diffuse through a dense layer of polymer on the particle surface, where its mobility will be restricted. Modification of the Smoluchowski equation for diffusion-controlled adsorption/desorption to account for this postulate led to the development of a model that gave excellent semi-quantitative agreement with experiment.

Chemically initiated dilatometric experiments (using three different types of initiator) gave the unusual result of very low reaction rates and low steady-state values of \bar{n} , the average number of radicals per particle. Using the standard kinetic equations for styrene-based systems (where it is assumed that an exited monomeric radical undergoes re-entry), this led to the calculation of impossibly small values of the entry rate coefficient ρ (far below any background or ‘thermal’ polymerization rate). However upon removing the assumption of re-entry and assuming that exited radicals undergo termination, the obtained values of ρ were in almost perfect agreement with the values predicted from the ‘control by aqueous phase growth’ entry mechanism.

This unexpected result was attributed to chemical reaction with the poly(acrylic acid) stabilizers through chain transfer to polymer (via hydrogen-atom abstraction). This postulate was verified by separate experiments that demonstrated that poly(acrylic acid) could act as a reasonably efficient chain transfer agent for styrene polymerization. The addition of poly(acrylic acid) to the

aqueous phase of a conventionally stabilized emulsion also led to the rate reduction seen previously. NMR experiments demonstrated the existence of poly(acrylic acid-*graft*-styrene), which could only be formed through termination of a poly(styrene) chain with a poly(acrylic acid) chain bearing a mid-chain radical (as the product of a chain transfer reaction).

These additional terms of transfer and termination were included in the governing kinetic equations of emulsion systems (the Smith-Ewart equations) to develop a model to account for the behaviour of electrosterically stabilized latexes. The ultimate fate of an exiting radical was now shown to be a competition between fates; successful desorption into the aqueous phase, or chemical reaction (through transfer or termination) within the hairy layer. These additional terms were shown to significantly reduce the theoretical value of \bar{n} , and were in excellent agreement with experiment. For small electrosterically stabilized particles with a densely packed ‘hairy layer,’ it was seen that transfer/termination is the dominant loss mechanism as opposed to desorption. The developed model showed that as the particle size was increased, the dominant loss mechanism once again became successful desorption into the aqueous phase. The model was shown to give excellent agreement with experimental data from ‘uncontrolled’ emulsion systems.

To explain the highly unusual secondary nucleation behaviour seen in systems such as these, it was postulated that beta-scission of a poly(acrylic acid) chain bearing a mid-chain radical is an important mechanistic step in the nucleation mechanisms of these systems. Modelling (both steady-state and time-dependent) gave good agreement with experiment with a minimal number of adjustable parameters. Theory (and supporting experimental evidence) demonstrated that this nucleation mechanism is only significant at high particle numbers; under other conditions the well-known ‘homogeneous nucleation’ mechanism is once again dominant.

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