RAFT in Emulsion Polymerization

A Two-Part Fugue of Theory and Experiment

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A thesis submitted in fulfillment of the requirements
for the degree of Doctor of Philosophy

School of Chemistry
University of Sydney
December 2003

Declaration of Originality

Chapter 3 of this thesis is reprinted from an article to which the author is a contributor. The experimental results reported in this Chapter are entirely the work of the author; the interpretation and presentation of these results was undertaken in collaboration with the coauthors of this paper. Sections of Chapters 1, 2 and 4 are based on a review article prepared by the author with the assistance of the coauthors of that review. Chapter 5 is reprinted from an article to which the author has sole authorship. Chapter 7 reports NMR data collected and analyzed by Dr Roger Mulder (CSIRO Molecular Science) from samples prepared by the author.

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Abstract

The free-radical polymerization of hydrophobic monomers in emulsions is an industrially and scientifically useful means of producing polymers. Resulting products from traditional emulsion polymerizations typically have quite wide distributions of molecular weights and even relatively simple architectures such as A–B blocks are impossible to synthesize. Reversible Addition-Fragmentation chain Transfer (RAFT) polymerization techniques allow unprecedented control over the molecular architecture of polymers made by free-radical polymerization. RAFT/emulsion polymerizations have considerable technical potential, for example to "tailor-make" material properties or to eliminate added surfactant from surface-coating formulations. However, considerable difficulties have been experienced in using RAFT in emulsion polymerization systems.

The successful use of the living radical polymerization technique RAFT is first described for the seeded emulsion polymerization of styrene using the benzyl-stabilized RAFT agent 2-phenylprop-2-yl phenyldithioacetate (PPPDTA). RAFT-mediated polymerization is seen to give both control over the molecular weight and a narrow polydispersity product. The presence of RAFT agent in the monomer droplets at the commencement of polymerization is postulated to be the cause of previous RAFT/emulsion attempts being unsuccessful. The use of γ-initiation of RAFT/emulsion systems is also described; the relaxation behavior on removal from the radiation source gives information about radical loss processes. A reduction in the rate of polymerization and long inhibition periods are observed that are dependent on the concentration of RAFT agent in both chemically- and γ-initiated systems. The characteristic times for γ-relaxations are also seen to be much shorter in the presence of RAFT agents.

Chain-length dependent termination is shown to play an important role in RAFT-mediated emulsion polymerization, with the RAFT agent changing the length of the propagating radical as a function of conversion. At low conversion, the termination rate coefficients are higher than in the absence of RAFT and zero-one kinetics is applicable to the system; at high conversion, termination is slower and pseudo-bulk kinetics are more appropriate. The observed increase in the number of radicals per particle as polymerization progresses is consistent with the influence of chain-length dependent termination, as is the observed increase in the timescale for relaxation with the increasing length of the dormant chains.

A method is described by which a suitable average rate coefficient for termination may be selected for the Smith–Ewart population balance equations. In some situations, it is possible to easily calculate the Smith–Ewart parameter for termination from the chain-length distribution of radicals analytically, while various numerical techniques (including integration and Monte Carlo simulation) may be used more generally.

RAFT/emulsion systems are shown to have greatly reduced compartmentalization compared to their non-RAFT analogues. The RAFT-induced exit of radicals was estimated to lead to a ~400-fold increase in the rate coefficient for radical exit from the particles, which is consistent with the rapid relaxations observed in γ-relaxation experiments.

The inhibition period of RAFT/emulsion systems is shown to be adequately modeled by zero-one kinetics, once the RAFT-induced exit of radicals, the exit of the re-initiating group from the particle, and the specificity of the re-initiating group to the initial RAFT agent are included.

With the models developed here for RAFT/emulsion systems, strategies for improving the performance of reactions are developed, including the use of lower-activity RAFT agents to improve the compartmentalization of the system. The use of oligomeric adducts to the initial RAFT agent are shown to improve the rate of polymerization by reducing the termination rate coefficients in the system.

Acknowledgements

Many people have contributed a lot to this project over the past four years from inception to completion. Their contributions ranged from teaching me experimental techniques to disbelieving my modeling results and from technical assistance to love and friendship. It would double the length of this thesis to thank everyone who has helped, but I will include as many here as I dare.

My heartfelt thanks to Bob Gilbert, Mat Ballard and Ezio Rizzardo who have been more than just supervisors over the course of this Ph.D. Your help, advice, friendship and wise counsel will always be appreciated and I hope to be able to provide the same in return. Sharing an office with Mat was daunting at first (how many Ph.D. students share an office with the boss?), but it was a great experience with many laughs and much computer-geeking.

The technical assistance and sounding board provided by Heng Taing was wonderful; I hope Heng learnt as much about the kinetics of polymer chemistry from me as I did about the stock market from him. Melissa Skidmore, Roshan Mayadunne and Amanda Finlay are thanked for their time spent patiently teaching me various experimental techniques. The many hours spent by Roger Mulder deciphering NMR spectra are much appreciated.

The numerous trans-Tasman discussions with Kim van Berkel and Greg Russell were greatly valued, as were the fruitful discussions with Greg Warr, John Quinn, Matthew Tonge, Malan Calitz and David Sangster. Chris Ferguson and Brian Hawkett, in particular, provided a constant source of critical appraisal of the modeling work in this project, making for many lively discussions about the exit of radicals from particles. The ever-thoughtful comments of Chris Fellows were also greatly appreciated. Thank you to all the members of the KCPC who made me so welcome each time I was in Sydney and at

Boomerang. The Key Centre for Polymer Colloids is established and supported under the Australian Research Council’s Research Centres Program.

The assistance of Michael Monteiro, Wieb Kingma and Christianne Gottgens during my time at the Technische Universiteit Eindhoven is gratefully acknowledged, as is the financial assistance of the Jim O’Donnell Young Scientist Prize from RACI Polymer Division to visit TUE. Thanks also to Stefan Bon and his group at the University of Warwick for their welcoming smiles for a traveling polymer chemist. The financial support of the University of Sydney Postgraduate Research Support Scheme for travel between Sydney and Melbourne and conference travel and registration is also thankfully acknowledged.

Dimitri Alexiev and David Sangster are thanked for their assistance with the γ-radiolysis experiments. Thanks also to the staff of the Lucas Heights Motel who did their best to provide a home-away-from-home-away-from-home during my visits to the Lucas Heights Science and Technology Centre. The γ-radiolysis experiments were made possible by the Australian Institute for Nuclear Science and Engineering.

The generous financial assistance of the Cooperative Research Centre for Polymers and permission to work at CSIRO Molecular Science in Clayton are also gratefully acknowledged. Thanks in particular to Tyson Clugg for help, friendship and advice, and to the many CSIRO staff who permitted me to subvert their computer resources in the name of science.

The sanity check provided by David Lamb throughout my time at the University of Sydney deserves special mention. Being friends since the beginning of first year, he has always taken the time to remind me just how sketchy things really are, as well as providing great ideas for experiments and little expeditions of theory. From the “MacGyver reactor” to Group Theory, it’s been a blast – thanks!

Tamara Paravicini and Kaylene Young were great flatmates at “Château Alma” over the first three years of my Ph.D.; the disturbing thought-experiment we used to discuss statistical analysis of data (irradiating bunnies in a γ-source) will haunt me for years to come. Living with scientists researching biological systems gave me a renewed appreciation for the physical sciences and just how nice styrene was as a system to study. I shall never complain about reproducibility problems again.

Peter Stiles (Macquarie University) also deserves many thanks for making the fateful decision to let me loose with a FORTRAN compiler during some work experience in theoretical chemistry in 1993. It was certainly the beginning of the end. My gratitude also to my high-school chemistry teacher Greg Nunan (1994–5), who provided much friendship and encouragement as I became transfixed on a career in chemistry.

Special thanks must go to my family. Anne Prescott, Mina Benzie and Ben Benzie have always encouraged me to challenge myself and to do my best at whatever I set my mind to, and I have so much to thank them for besides. I believe this thesis is a shining example of what they have taught me to do. Thanks also to Terry, Christina and Phil Hart who welcomed me into their home when I moved to Melbourne and provided much love as I “pushed back the frontiers of knowledge”.

Last, but most importantly, my deepest gratitude goes to Judy Hart. The excitement of working on this project has certainly been added to with our adventures buying a home, renovating and getting married all at the same time. Thank you for making me smile, helping me solve differential equations and giving me a hug when I needed one; I hope that I do just as well when it is my time to return the favor.

To everyone who has been a part of this project… thank you!

Stuart Prescott

Publications

Parts of this work have been published in the following journal articles:

S. W. Prescott, M. J. Ballard, E. Rizzardo, R. G. Gilbert

RAFT in Emulsion Polymerization: What Makes It Different.

Aust. J. Chem., **2002**, *55*, 415.

S. W. Prescott, M. J. Ballard, E. Rizzardo, R. G. Gilbert

Successful Use of RAFT Techniques in Seeded Emulsion Polymerization of Styrene: Living Character, RAFT Agent Transport and Rate of Polymerization.

Macromolecules, **2002**, *35*, 5417.

S. W. Prescott, M. J. Ballard, E. Rizzardo, R. G. Gilbert

RAFT Techniques in Emulsion Polymerization: Rate of Polymerization and Radical Phase Transfer Events.

Polymer Preprints, **2002**, *43*, 146.

S. W. Prescott

Chain-Length Dependence in Controlled/Living Radical Polymerizations: Physical Manifestation and Monte Carlo Simulation of Reversible Transfer Agents.

Macromolecules, **2003**, *ASAP*, DOI: 10.1021/ma034845h.

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Glossary of Symbols and Abbreviations

symbol	**definition**	**typical units**
a	root-mean-square end-to-end distance per square root of the number of monomer units in the polymer chain	nm
A	ratio between the rate of conversion and $\overline{n}$ (in analysis of Interval II data)	
A	ratio between the pseudo-first-order rate of conversion (*i.e.* $\mathrm{d}[-\ln(1-x)]/\mathrm{d}t$) and $\overline{n}$ (in analysis of Interval III data)	
AA	acrylic acid (monomer)	
ATRP	atom-transfer radical polymerization	
BA	butyl acrylate (monomer)	
c	Smith–Ewart pseudo-first-order rate coefficient for the (second-order) annihilation of radicals	s^{-1}
$c(t'')$	abbreviation of $c(t, t', t'')$	s^{-1}
$c(t, t', t'')$	parameter c (as above) in a doubly-distinguished particle N_2'' with a dependence on t, t', and t''.	s^{-1}
$c_0(t)$	normalization of $\overline{c}(t)$	s^{-1}
c_F	contraction factor in dilatometry calculations	$\mathrm{cm}^3\ \mathrm{g}^{-1}$
c_rd	contribution of reaction-diffusion to c	s^{-1}
c_trM	contribution of transfer to monomer to c	s^{-1}
c^1L	pseudo-first-order rate coefficient for the termination of a monomeric radical with a long radical	s^{-1}
c^SL	pseudo-first-order rate coefficient for the termination of a short radical with a long radical	s^{-1}
$\overline{c}(t)$	instantaneous value of c, averaged over the chain-length distribution of all radicals present in the system	s^{-1}
c^*	concentration of polymer where chains overlap	$\mathrm{mol\ dm}^{-3}$
c^{**}	concentration of polymer where chains are entangled	$\mathrm{mol\ dm}^{-3}$
C_1	normalization for the time-evolution of N_2'' species	
C_w	concentration of monomer in the aqueous phase	$\mathrm{mol\ dm}^{-3}$
C_w^R	concentration of the species R in the aqueous phase	$\mathrm{mol\ dm}^{-3}$
$C_\mathrm{w}^\mathrm{sat}$	saturation concentration of monomer in the aqueous phase	$\mathrm{mol\ dm}^{-3}$

C_p	concentration of monomer in the particles	mol dm^{-3}
C_p^R	concentration of the species R in the particle phase	mol dm^{-3}
$C_\mathrm{p}^\mathrm{sat}$	saturation concentration of monomer in the particles	mol dm^{-3}
C_tr	transfer constant for a polymeric radical with an RTA, $C_\mathrm{tr} = k_\mathrm{tr,RAFT}/k_\mathrm{p}$	
$C_{-\mathrm{tr}}$	transfer constant for an R$^\bullet$ radical with an RTA, $C_{-\mathrm{tr}} = k_{-\mathrm{tr,RAFT}}/k_\mathrm{add}^\mathrm{R}$	
C_z	concentration of dormant *z*-meric radicals in a particle	mol dm^{-3}
CHDF	capillary hydrodynamic fractionation (method for determining particle size)	
CLD	chain length dependent	
d_m	density of monomer	g cm^{-3}
d_p	density of polymer	g cm^{-3}
D	dormant chain	
D_i	dormant chain of length *i*	
$\mathrm{D_P}$	dormant chain with a polymeric leaving group (*i.e.* dormant polymeric chain)	
$\mathrm{D_R}$	dormant species with an R group (*i.e.* initial RAFT agent)	
D_1	diffusion coefficient of the monomeric radical in a particle	cm^2 s^{-1}
$D_i(N)$	instantaneous chain-length distribution of the dormant chains in a particle with *i* radicals	
D_w	diffusion coefficient of the monomeric radical in water	cm^2 s^{-1}
D^{ij}	mutual diffusion coefficient for an *i*-meric and *j*-meric chain	cm^2 s^{-1}
D^rd	diffusion coefficient for the chain end for reaction-diffusion	cm^2 s^{-1}
D_i	abbreviation for D_i^com	cm^2 s^{-1}
D_i^com	center-of-mass diffusion coefficient of an *i*-mer	cm^2 s^{-1}
D_R	diffusion coefficient of the species R (or R$^\bullet$) in water	cm^2 s^{-1}
D_w^R	diffusion coefficient of the species R (or R$^\bullet$) in water	cm^2 s^{-1}
D_IR	mutual diffusion coefficient for non-identical initiator-derived radicals for "hetero-termination"	cm^2 s^{-1}
D_II	mutual diffusion coefficient for identical initiator-derived radicals for "homo-termination"	cm^2 s^{-1}

DRI	differential refractive index; commonly used response from GPC instrument	
$E^\bullet$	exited monomeric radical	
[E]	concentration of exited monomeric radicals	mol dm^{-3}
ESR	electron spin resonance (method for identifying and quantifying the radicals present)	
f	initiator efficiency in emulsion polymerization, calculated from Maxwell–Morrison theory for entry	
f_{ll}	fraction of all termination reactions that are long–long	
$f_{z\mathrm{l}}$	fraction of all termination reactions that are *z*-meric–long	
$G_i(N)$	instantaneous chain-length distribution of the radicals in a particle with *i* radicals	
GPC	gel permeation chromatography, also known as size exclusion chromatography; method for determining the molecular weight distribution	
h_t	height of the meniscus in the capillary at any given time, relative to the initial height	µm
h_{100}	height of the meniscus in the capillary relative to the initial height at 100% conversion	µm
i	integer (*e.g.* for chain length or number of radicals in a particle)	
I–I	undecomposed initiator molecule	
I	initiator molecule	
$I^\bullet$	decomposed initiator fragment	
$IM_i^\bullet$	polymeric or oligomeric radical with degree of polymerization *i*	
j	integer (*e.g.* for chain length)	
j_{crit}	critical degree of polymerization for chain collapse	
k	(as a subscript or superscript) integer (*e.g.* for chain length)	
k	Smith–Ewart pseudo-first-order rate coefficient for the desorption of radicals from particles	s^{-1}
$k_{\mathrm{a}z}$	second-order rate coefficient for the adsorption of a *z*-meric radical onto the surface of a particle from the aqueous phase	dm^3 mol^{-1} s^{-1}

k_{ads}	second-order rate coefficient for the adsorption of a monomeric radical onto the surface of a particle from the aqueous phase	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
$k_{\mathrm{add}}^{\mathrm{R}}$	second-order rate coefficient for the addition of the RAFT re-initiating radical ($\mathrm{R}^{\bullet}$) to monomer	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
k_{cr}	pseudo-first-order rate coefficient for radical exit assuming the complete re-entry of exited radicals	s^{-1}
k_{ct}	pseudo-first-order rate coefficient for radical exit assuming the complete aqueous-phase termination of radicals	s^{-1}
k_{dM}	first-order rate coefficient for the desorption of a monomeric radical from a particle into the aqueous phase	s^{-1}
k_{dz}	first-order rate coefficient for the desorption of a *z*-meric radical from a particle into the aqueous phase	s^{-1}
k_{d}	first-order rate coefficient for the dissociation of initiator	s^{-1}
k_{dR}	first-order rate coefficient for the desorption of an $\mathrm{R}^{\bullet}$ radical from a particle into the aqueous phase	s^{-1}
k_{exit}	first-order rate coefficient for the exit of radicals from a particle	s^{-1}
k_{e}^{z}	second-order rate coefficient for the entry of a *z*-meric radical into a particle	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
$k_{\mathrm{e}}^{\mathrm{R}}$	second-order rate coefficient for the entry of a exited $\mathrm{R}^{\bullet}$ radical into a particle	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
k_{p}	second-order rate coefficient for propagation	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
k_{pI}	second-order rate coefficient for addition of the initiator-fragment, $\mathrm{I}^{\bullet}$, to monomer	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
k_{p}^{i}	second-order rate coefficient for propagation of a *i*-mer	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
$k_{\mathrm{p,aq}}^{i}$	second-order rate coefficient for aqueous phase propagation of a *i*-mer	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
k_{t}	second-order rate coefficient for the termination of radicals in the particles, usually meaning average rate coefficient $\langle k_{\mathrm{t}} \rangle$	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
$\langle k_{\mathrm{t}} \rangle$	average second-order rate coefficient for the termination of radicals in the particles; average is over distribution of radicals	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$
$k_{\mathrm{t,aq}}$	second-order rate coefficient for radical termination in the aqueous phase	$\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$

$k_{\mathrm{t,aq}}^{\mathrm{R}}$	second-order rate coefficient for radical termination between two non-identical initiator-derived radicals in the aqueous phase	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
k_{t}^{ij}	second-order rate coefficient for radical termination between an *i*-meric radical and a *j*-meric radical	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{t}}^{\text{long-long}}$	second-order rate coefficient for radical termination between two long radicals	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{t}}^{\text{short-long}}$	second-order rate coefficient for radical termination between a short radical and a long radical	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{t}}^{\text{short-short}}$	second-order rate coefficient for radical termination between two short radicals	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
k_{tr}	second-order rate coefficient for the transfer to monomer	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{tr,D}}$	second-order rate coefficient for the transfer to a dormant species	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{tr,RAFT}}$	second-order rate coefficient for the transfer of radical activity to a dormant RAFT species	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{\mathrm{tr,RAFT}}^{1}$	second-order rate coefficient for the transfer of radical activity to the initial RAFT species	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
$k_{-\mathrm{tr,RAFT}}$	second-order rate coefficient for the transfer of radical activity from an $\mathrm{R}^{\bullet}$ radical to a dormant RAFT species	$\mathrm{dm^3\ mol^{-1}\ s^{-1}}$
long	indicates that the length of the species is such that entanglement is important and diffusion is slow ($\gtrsim 40$)	
L	indicates that the length of the species is “long”	
m	length of a radical chain in zero-one-two theory	
m_{mon}	mass of monomer	g
m_{p}	mass of polymer	g
M	monomer unit	
$\mathrm{M}^{\bullet}$	monomeric radical	
M_0	molecular mass of a monomer unit	
$\overline{M}_{\mathrm{n}}$	number-average molecular weight	
$\overline{M}_{\mathrm{n}}^{\mathrm{pred}}$	predicted number-average molecular weight	
$\overline{M}_{\mathrm{w}}$	weight-average molecular weight	
MMA	methyl methacrylate (monomer)	
MWD	molecular weight distribution	

n	length of a radical chain in zero-one-two theory	
n_{D}	number of D species in a particle	
$n_{\mathrm{I}}^{\mathrm{f}}$	final amount of initiator in the system	mol
$n_{\mathrm{I}}^{\mathrm{i}}$	initial amount of initiator in the system	mol
n_{I}	number of initiator-derived radicals denoted "*i*-mers" for the "homo-termination" reaction	
n_{R}	number of initiator-derived radicals not denoted "*i*-mers" for the "hetero-termination" reaction	
n_k^{D}	number of D_k species in the particle	
n_{m}^0	amount of monomer per unit volume of aqueous phase	$\mathrm{mol\ dm^{-3}}$
n_{RAFT}	number of moles of RAFT agent added	mol
n_{ZX}	number of dormant *z*-meric species (ZX) per particle	
$\overline{n}$	average number of radicals per particle	
$\overline{n}_{\mathrm{i}}$	initial $\overline{n}$ in a system (steady state before relaxation)	
$\overline{n}_{\mathrm{sp}}$	$\overline{n}$ in a system with only spontaneous initiation	
$\overline{n^2}$	average of the square of the number of radicals per particle	
N_0	number concentration of particles containing no radicals	$\mathrm{dm^{-3}}$
N_1^{p}	number concentration of particles containing one polymeric radical	$\mathrm{dm^{-3}}$
N_1^{R}	number concentration of particles containing one $\mathrm{R}^{\bullet}$ radical	$\mathrm{dm^{-3}}$
$N_2''(t'')$	abbreviation of $N_2''(t, t', t'')$, the population of doubly distinguished particles, normalized so that $\sum N_i = 1$	
N_{A}	Avogadro constant	$\mathrm{mol^{-1}}$
N_{c}	number concentration of particles in the aqueous phase	$\mathrm{dm^{-3}}$
N_i	population of particles with *i* polymeric radicals, normalized so that $\sum N_i = 1$	
N_i	number concentration of particles with *i* polymeric radicals (normalized such that $\sum N_i = N_{\mathrm{c}}$)	$\mathrm{dm^{-3}}$
NMP	nitroxide-mediated polymerization	
NMR	nuclear magnetic resonance (method for identifying the chemical species present, esp. for organic compounds)	
p^{ij}	probability that an *i*-meric radical will terminate with a *j*-meric radical in an encounter	

$\mathrm{P}^\bullet$	polymeric radical	
P_j	probability of an entering radical consuming at least *j* monomer units before termination	
$P_j(t)$	probability of an entering radical consuming at least *j* monomer units before termination, as measured at a given time *t* (hence w_p) since the system reached a (quasi-) steady state	
P_n	polymeric chain with degree of polymerization *n*	
$\mathrm{P}_n^\bullet$	polymeric radical with degree of polymerization *n*	
$P(A)$	probability of event "*A*" occurring (*e.g.* $P(\mathrm{P}^\bullet + \mathrm{M})$ is the probability of the propagation reaction occurring)	
P(exit-M)	probability of a $\mathrm{M}^\bullet$ species exiting a particle	
P(exit-Z)	probability of a *z*-meric radical exiting a particle	
PD	polydispersity of the polymer sample PD = $\overline{M}_\mathrm{w}/\overline{M}_\mathrm{n}$	
PLP	pulse laser polymerization experiment (to determine k_p, k_t etc.)	
PPPDTA	RAFT agent 2-phenylprop-2-yl phenyldithioacetate: $\mathrm{Ph{-}C(CH_3)_2{-}S{-}C({=}S){-}CH_2{-}Ph}$	
r	radius of a particles	nm
r_c	radius of the capillary in the dilatometry experiment	mm
r_I	interaction radius of radicals denoted "*i*-mers" for the "homo-termination" reaction	
r_R	interaction radius of radicals denoted "*i*-mers" for the "hetero-termination" reaction	
r_s	swollen radius of the particles	nm
r_u	unswollen radius of the particles	nm
R	leaving group (re-initiating group) of the RAFT agent	
$\mathrm{R}^\bullet$	re-initiating radical	
$\mathrm{R}^\bullet$	generic radical species (Maxwell–Morrison theory)	
R^2	measure of goodness of fit, esp. for linear fits	
$R_\mathrm{coll}^\mathrm{I+I}$	rate of collision of identical radicals leading to the "homo-termination" reaction, $\mathrm{IM}_i^\bullet + \mathrm{IM}_i^\bullet$	mol dm^{-3} s^{-1}
$R_\mathrm{coll}^\mathrm{I+R}$	rate of collision of non-identical radicals leading to the "hetero-termination" reaction, $\mathrm{IM}_i^\bullet + \mathrm{R}^\bullet$	mol dm^{-3} s^{-1}

$R_{\mathrm{rxn}}^{\mathrm{I+I}}$	rate of “homo-termination”, $\mathrm{IM}_i^\bullet + \mathrm{R}^\bullet$	mol dm^{-3} s^{-1}
$R_{\mathrm{rxn}}^{\mathrm{I+R}}$	rate of “hetero-termination”, $\mathrm{IM}_i^\bullet + \mathrm{R}^\bullet$	mol dm^{-3} s^{-1}
R_{p}	rate of polymerization	mol dm^{-3} s^{-1}
RAFT	reversible addition-fragmentation chain transfer	
RTA	reversible transfer agent, *e.g.* a RAFT agent	
short	indicates that the length of the species is such that entanglement is unimportant and diffusion is fast ($\lesssim$ 10)	
Sty	styrene (monomer)	
SEC	size exclusion chromatography, see GPC	
t	time during a reaction, measured either from when the initiator was added (assuming no inhibition) or from when the system was removed from the γ-source	s
t	time since the reaction reached a (quasi-) steady state (in the case of zero-one-two theory)	s
t'	time for which a distinguished radical grew in a particle with one radical	s
t''	time that the two distinguished radicals coexist	s
t_{z}	time adjustment to account for the entering radical having non-zero length (equivalent to the age of a z-meric radical were it to grow within the particle)	s
T	temperature	K or °C
T_{R}	total concentration of radical species in the aqueous phase able to undergo termination reactions	mol dm^{-3}
THF	tetrahydrofuran, the solvent used for GPC molecular weight determination	
U_i	uniform random deviate (number) on the interval [0,1]	
UV-Vis	ultra-violet/visible spectroscopy (method for quantifying the amount of a chromophore present)	
V_0	initial volume of the reaction mixture in the dilatometer	dm^3
V_{aq}	volume of the aqueous phase in the reactor	dm^3
V_{m}	volume of monomer used	cm^3
V_{s}	swollen volume of a particle	dm^3
V_{t}	volume of the reaction mixture in the dilatometer at a time t, calculated from the height of the meniscus h_t	dm^3

w_p	weight fraction of polymer in the system	
x	fractional conversion of monomer to polymer	
$x^{\mathrm{II/III}}$	conversion at which monomer droplets disappear (Interval II to Interval III transition)	
X	chemical symbol representing the dormant end cap on a chain (in the case of RAFT, the thiocarbonylthio group)	
X_d	length of the dormant chains in the system	
$\bar{X}_{\mathrm{n,d}}$	number average degree of polymerization	
z	critical degree of polymerization for a chain to become surface active	
Z	activating group of the RAFT agent	
ZX	dormant z-meric chain $^{-}\mathrm{IM}_z{-}\mathrm{X}$	
α	fate parameter for exited radicals on $[-1,1]$	
β	exponent for the chain-length dependence of the diffusion of polymeric species (in general, may be a function of w_p, hence of t); physical values are $\beta \in [0,2]$	
χ_R	mole fraction of the species R	
Δ_i	CLD sum of the frequency of all events that may occur to an i-meric radical in a particle	
$\bar{\Delta}_\mathrm{m}$	average change in the number of monomer units in a particle as a result of a radical entering the particle	
δt_{max}	maximum deviation from the current time which is permissible in a Monte Carlo simulation	s
γ	γ-radiation from a ^{60}Co radioactive source	
$\Gamma(b, z)$	incomplete gamma function, $\Gamma(b, z) = \int_z^\infty t^{b-1} e^{-t}\,\mathrm{d}t$	
ρ	Smith–Ewart pseudo-first-order rate coefficient for the entry of radicals into particles	s^{-1}
ρ_i	pseudo-first-order rate coefficient for the entry of initiator derived radicals into a particle	s^{-1}
ρ_m	density of monomer	$\mathrm{g\ cm}^{-3}$
ρ_p	density of polymer	$\mathrm{g\ cm}^{-3}$
ρ_{spon}	pseudo-first-order rate coefficient for the entry of spontaneously generated radicals into a particle, sometimes denoted ρ_{thermal}	s^{-1}

ρ_t	pseudo-first-order rate coefficient for the entry of all radicals into a particle	s^{-1}
σ	interaction radius for the reaction of two radicals	nm
τ	average time-step of a process	s
% w/w	percentage contents of a material on a weight-in-weight basis	
$[a,b]$	interval described by x where $a \le x \le b$	
$\{a, b, \ldots\}$	set containing elements a, b, etc.	
$\approx$	is approximately equal to	
$\gg$	is much greater than	
$\not\gg$	is **not** much greater than	
$\ll$	is much less than	
$\not\ll$	is **not** much less than	
$\prod_{i=a}^{b} f(i)$	product of $f(i)$ for all $i \in [a,b]$, where a and b are integers	
$\sum_{i=a}^{b} f(i)$	sum of $f(i)$ for all $i \in [a,b]$, where a and b are integers	