Progress in Polymer Science xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Progress in Polymer Science

journal homepage: www.elsevier.com/locate/ppolysci

The strength of multi-scale modeling to unveil the complexity of radical polymerization

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ARTICLE INFO

Article history:
Received 7 June 2015
Received in revised form 17 March 2016
Accepted 5 April 2016
Available online xxx

Keywords:
Controlled radical polymerization
Free radical polymerization
Multi-scale modeling
Chain length distribution
Particle size distribution
Ab initio

ABSTRACT

The strength of multi-scale modeling to support the fundamental understanding and design of radical polymerization processes is illustrated, considering both controlled and free radical polymerization (CRP/FRP) in non-dispersed (bulk/solution) and dispersed (suspension/emulsion) media. At the molecular scale, the importance of joint experimental and theoretical studies is highlighted. At the micro-scale, the concept of apparent rate coefficients is elaborated to account for the possible influence of diffusional limitations on the local reaction rates. At the meso-scale, the key characteristics to fundamentally describe the evolution of the particle size distribution are covered and the possible interaction with the micro- and macro-scale is discussed. At the macro-scale, the main mathematical tools to assess the relevance of mixing and temperature gradients are provided. Several examples on CRP and FRP processes are included to showcase the modeling capabilities for each scale, focusing both on laboratory and industrial reactors.

Contents

Abbreviations: ARGET, activators regenerated by electron transfer; ATRP, atom transfer radical polymerization; CLD, chain length distribution; CFD, computational fluid dynamics; CRP, controlled radical polymerization (also known as RDRP); *cmc*, critical micelle concentration; COSMO-RS, conductor-like screening model for realistic solvents; CTA, chain transfer agent; CSTR, continuous stirred tank reactor; DMSO, dimethyl sulfoxide; DPMA, 2,2-dimethoxy-2-phenylacetophenone; DoPAT, 2-(dodecylthiocarbonothioylthio)propanoic acid; DFT, density functional theory; ESR, electron spin resonance; FRP, free radical polymerization; ICAR, initiators for continuous activator regeneration; MMA, methyl methacrylate; LCB, long chain branching; LDPE, low density polyethylene; MDSD, monomer droplet size distribution; MMA, methyl methacrylate; ME_6TREN, tris(dimethylamino) ethyl amine; *n*BuA, n-butyl acrylate; NMP, nitroxide mediated polymerization; PLP, pulsed laser polymerization; PMDETA, N,N′,N″,N″-pentamethyldiethylenetriamine; PSD, particle size distribution; PVC, poly(vinyl chloride); RAFT, reversible addition fragmentation chain transfer; RAFT-CLD-T, RAFT-chain length dependent-termination technique; RDRP, reversible deactivation radical polymerization (also known as CRP); SARA, supplementary activator and reducing agent; SCB, short chain branching; SEC, size exclusion chromatography; SET-LRP, single electron transfer-living radical polymerization; SG1, N-(2-methyl-2-propyl)-N-(1-diethylphosphono-2,2-dimethylpropyl)-N-oxyl; S-2-EP-OEX, (S)-2-(Ethyl propionate)-(O-ethyl xanthate); TEMPO, 2,2,6,6-tetramethylpiperidinyloxyl; VC, vinyl chloride; VTST, variational transition state theory.

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http://dx.doi.org/10.1016/j.progpolymsci.2016.04.002
0079-6700/

List of symbols

Roman symbols

A	pre-exponential factor for chemical reaction, $(m^3\ mol^{-1})\ s^{-1}$
A_i $(i = 1, 2)$	molecule, –
A_1A_2	encounter pair of molecules A_1 and A_2, –
$B(V,t)$	"birth function" for PSD calculation, $m^{-3}\ s^{-1}$
C	molecule, –
C_i $(i = 1, 2)$	adjustable parameter for correlation
$Cu(I)X$	ATRP activator, –
$Cu(II)X_2$	ATRP deactivator, –
d_p	particle diameter, m
$D(V,t)$	"death function" for PSD calculation, $m^{-3}\ s^{-1}$
$D_{u/v}$	diameter of particle with volume U/V, m
D_{Ai}	diffusion coefficient of molecule A_i, $m^2\ s^{-1}$
$D_{A1,0}$	pre-exponential factor for diffusion coefficient of molecule A_1, $m^2\ s^{-1}$
E_A	activation energy, $J\ mol^{-1}$
g	breakage rate coefficient, s^{-1}
$\boldsymbol{g}$	gravity vector, m s
G	growth rate of a particle, $m^3\ s^{-1}$
h	Planck constant, J s
i	chain length, –
i_s	*s*th inflection point in characteristic PLP CLD, –
I_2	conventional radical initiator, –
F	volumetric flow rate, $m^3\ s^{-1}$
$F_{A,inst}$	instantaneous average copolymer composition for A monomer units, –
f_A	molar fraction of monomer A in monomer feed, –
k	rate coefficient, $(m^3\ mol^{-1})\ s^{-1}$
k_B	Boltzmann constant, $J\ K^{-1}$
k'	coalescence coefficient, $m^3\ s^{-1}$
P	dead polymer molecule, –
P'	pressure, Pa
K_{eq}	activation/deactivation equilibrium coefficient, $(mol\ m^{-3}$ or –)
K_{ij}	hole free volume parameter, $m^3\ kg^{-1}\ K^{-1}$ or K
M	monomer molecule, –
MM_m	monomer molar mass, $kg\ mol^{-1}$
$n(V,t)$	number density function per volume unit, m^{-6}
n	molecularity of the reaction, –
$\bar{n}$	average number of radicals per particle, –
N_A	Avogadro constant, mol^{-1}

Please cite this article in press as: D'hooge DR, et al. The strength of multi-scale modeling to unveil the complexity of radical polymerization. Prog Polym Sci (2016), http://dx.doi.org/10.1016/j.progpolymsci.2016.04.002