



A deterministic model for positional gradients in copolymers

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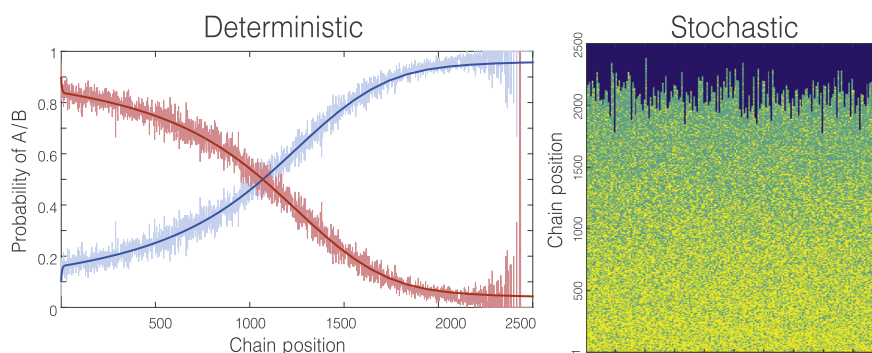
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HIGHLIGHTS

- Mathematical model that captures compositional profiles of copolymer chains.
- The model aids in designing polymer chains closest to a specified composition pattern.
- Quality measure indicates deviations from the ideal gradient standard.

GRAPHICAL ABSTRACT



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ABSTRACT

A deterministic modelling approach is developed to predict the internal structure of gradient copolymer chains. A key innovation of the modelling approach is the introduction of a positional variable that gives direct access to quantitative gradient characteristics: the ensemble average composition and the gradient deviation. This positional variable is used to develop multi-dimensional population balance equations that can be solved numerically to calculate gradient quality measures. The methodology is illustrated using the gradient copolymerisation of ethylene and 1-octene via coordinative chain transfer mechanism, which is representative of a variety of polymerisation schemes for gradient copolymers. Simulation results are validated with those obtained by stochastic simulations which, until now, were the only means of predicting detailed gradient quality.

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1. Introduction

Living polymerisation systems are attractive because they permit careful control of microstructural properties of polymer chains. An important class of materials that can be produced via living

polymerisation is gradient copolymers (Pakula and Matyjaszewski, 1996; Beginn, 2008; Li et al., 2015). Gradient copolymers are similar to block copolymers, but without sharp boundaries between chain blocks. The more gradual gradient structure causes different physical properties in comparison to block copolymers, so that a variety of high-added-value products can be made (Pakula and Matyjaszewski, 1996; Beginn, 2008; Li et al., 2015, 2014b; Zhao et al., 2011; Li and Luo, 2014; Zhou

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Nomenclature

List of symbols

χ	conversion of monomers	M_n	number-average molecular weight
χ^{tar}	target conversion	M_w	weight-average molecular weight
$\lambda(x, t)$	chain length distribution	M_w^{tar}	target weight-average molecular weight
$\lambda_{dm}(t)$	total concentration of dormant chains ending with $m \in \{a, b\}$ at catalyst	$M_{x,y}$	monomer that at the position y of a dead chain of length x
$\lambda_{rm}(t)$	total concentration of growing chains ending with $m \in \{a, b\}$ at catalyst	$M_{x,y}^{d,a}$	monomer that at the position y of a dormant chain of length x , ending with A at catalyst
$\mu(x, y, t)$	concentration of A monomers at position y of chains with length x	$M_{x,y}^{d,b}$	monomer that at the position y of a dormant chain of length x , ending with B at catalyst
C	initiator	$M_{x,y}^{r,a}$	monomer that at the position y of a living chain of length x , ending with A at catalyst
C*	initiator radical	$M_{x,y}^{r,b}$	monomer that at the position y of a living chain of length x , ending with B at catalyst
$c_a, c_b(t)$	concentrations of unreacted monomers A and B	$p_a(t)$	total concentration of reacted monomers of type A in the polymer
$c_{b,\text{init}}$	initial concentration of B monomer	$P_a(x, y, t)$	the fraction of polymer chains of length x that contain monomer A at position y
$c_{\text{cat},\text{init}}$	initial concentration of catalyst	$P_a(y, t)$	probability that a randomly selected chain has monomer A at position y
$c_{\text{cta},\text{init}}$	initial concentration of CTA	P_x	dead chain of length x
$c_{\text{cta}}(t)$	concentration of the chain transfer agent	$P_x^{d,a}$	dormant chain of length x , ending with A at catalyst
$c_s(t)$	concentration of activated initiator	$P_x^{d,b}$	dormant chain of length x , ending with B at catalyst
f_a	initial fraction of monomer concentration	$P_x^{r,a}$	living chain of length x , ending with A at catalyst
k_{aa}	a homo-propagation rate constant	$P_x^{r,b}$	living chain of length x , ending with B at catalyst
k_{ab}	AB cross-propagation rate constant	t_{end}	reaction time
k_a	active site formation rate constant	x	chain length
k_{ba}	BA cross-propagation rate constant	y	chain position
k_{bb}	B-homo-propagation rate constant		
k_{cs}	transfer to virgin CTA rate constant		
k_{cs}	transfer to polymeryl CTA rate constant		
k_i	initiation rate constant		
k_{th}	thermal termination rate constant		

et al., 2013). Gradient copolymers have been produced using different radical polymerisation mechanisms including anionic, cationic, and controlled radical polymerisation methods (Beginn, 2008; Li et al., 2015). For example, the group of Li and Zhu used a model-based approach with both RAFT (reversible addition fragmentation transfer) and ATRP (atom transfer radical polymerization) to design semi-batch feeding strategies that produce copolymer chains designed to have uniform, linear and hyperbolic gradients (Sun et al., 2007, 2008; Li et al., 2014a; Zhao et al., 2009). Their deterministic models, which were used to select the appropriate reactor operating conditions relied on the method of moments to provide reasonably accurate predictions of M_n , polydispersity, and conversion versus time behaviour for the comonomers. Similarly, Ye and Schork developed a method-of-moments model to predict changes in M_n , M_w and copolymer composition, as well as average sequence length during semi-batch RAFT and nitroxide mediated radical copolymerisations (Ye and Schork, 2009, 2010). Their RAFT model was then used to develop optimal semi-batch feeding policies to produce gradient copolymers with linear composition profiles. The models from these two research groups account for chain termination (and in some cases chain transfer) reactions that influence molecular weight distribution (MWD) and disrupt gradient quality. However, their deleterious influence on the quality of the gradient copolymers was largely ignored.

In contrast, Fortunatti et al. (2014) developed a more detailed deterministic model to describe nitroxide mediated radical copolymerisation of styrene and α -methylstyrene in semibatch reactors. Their model, which accounts for termination and chain transfer, uses probability generating functions to predict the joint distribution of the number of styrene and α -methylstyrene units within the copolymer chains (in addition to M_n , M_w and instantaneous copolymer composition). This modelling approach provides helpful information about variability within the population of the copolymer chains produced under different operating conditions. For

instance, Fortunatti's model can predict the proportion of low- M_n styrene-rich copolymer that forms under different operating conditions. Fortunatti's model, however, does not provide information about how the comonomer units are distributed along the copolymer chains.

Zhang et al. (2010) developed a deterministic model to describe semi-batch production of olefin gradient copolymers via Coordinative Chain Transfer Polymerization (CCTP). Zhang's model is similar to several of the reversible-deactivated radical copolymerization models described above, in that it accounts for the influence of chain transfer and thermal termination reactions on M_n and M_w , but does not account for the influence of these side reactions on gradient copolymer quality (i.e., on the position of the comonomer units along individual chains).

One advantage of the deterministic modelling approaches, when compared with Monte Carlo methods, is that they result in straightforward sets of dynamic balance equations to describe the reacting systems of interest. A second advantage is that the computational effort required to obtain numerical solutions is usually very small, compared with Monte Carlo models, especially if special techniques are used to reduce the number of balance equations that needs to be solved. Some examples of such techniques include the method of moments (Ye and Schork, 2009, 2010; Zhang et al., 2013), projection methods (Kryven and Iedema, 2013, 2014a; Kryven et al., 2015), and parametrisation with degree distribution (Schamboeck et al., 2017; Kryven, 2017a,b,c, 2016).

A number of research groups have used KMC models to describe gradient copolymer production via CCTP and a variety of reversible-deactivated radical copolymerisation technologies (Pakula and Matyjaszewski, 1996; Van Steenberge et al., 2012; Valente et al., 2013; Mohammadi et al., 2014; Al-Harathi et al., 2009). The main benefit of the KMC approach is that it permits explicit tracking of a large number of individual copolymer chains, making it relatively easy, compared to deterministic methods,

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