PREDICTING COPOLYMER PROPERTIES - SEQUENCE LENGTH AND GRADIENT QUALITY

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Abstract

A multidimensional population balance modeling approach is presented accounting for chain length, copolymer composition, sequence length and gradient distribution. This is demonstrated on radical copolymerization of styrene and acrylonitrile and on chain shuttling copolymerization (CSP) of ethylene and 1-octene.

Keywords

Population balance, copolymerization, sequence length, gradient copolymer

Introduction.

Block and gradient copolymers have traditionally been at the forefront of research focused on creating nano-structured polymers. It is known that the sequence template of a block copolymer chain drives the formation of locally segregated domains. Depending on the chemical and physical nature of the system, the sequence of blocks in a single chain may obey various patterns. Considering an A/B system copolymerized chain structures are: random chains with constant probability of inclusion of A or B monomer at every position; gradient chains with probability of A (or B) inclusion gradually increasing with position in the chain; pure chains that consist of only A or B. In a batch reactor the system may switch producing polymer chains of each kind. The new mathematical framework describes the evolution of a sequence length distribution for radical copolymerization of styrene (A) and acrylonitrile (B)\textsuperscript{1}. In addition, we have developed a tool describing gradient quality of copolymers using the concept of the ensemble average of local chain composition, an unambiguous gradient measure\textsuperscript{2,3}. This is demonstrated on a case of chain shuttling polymerization of ethylene (A) with 1-octene (B).

Sequence modeling in styrene (A)/acrylonitrile (B) copolymerization.

We have designed a framework for constructing population balance equations (PBE) for sequences (see Figure 1). $O^{a}_{x,y}$ ($O^{b}_{x,y}$) denote ‘open sequences’ of y monomers of type A (B) and are located at the radical end of a living chain of length x. ‘Closed sequences’, $C^{a,a}_{x,y}$ ($C^{a,b}_{x,y}$, $C^{b,a}_{x,y}$, $C^{b,b}_{x,y}$) are located at a non-terminal position: any position in a living chain except the radical end. The top indices refer to the monomer the sequence is composed, resp. the last monomer (radical) in the living chain. ‘Dead’ sequences in dead chains are on terminal or nonterminal positions: $Q^{a}_{x,y}$ ($Q^{b}_{x,y}$). These sequences undergo changes due to the copolymerization reactions. Initiation produces open sequences of length 1, e.g. $A + I \rightarrow O^{a}_{1,1}$. If an open sequence of a certain type (a or b, upper index) propagates with a monomer of the same type, both the sequence length and the total chain length are increased, e.g. $O^{a}_{x,y} + A \rightarrow O^{a}_{x+1,y+1}$. If an open sequence propagates with a monomer of a different type, it changes into a closed sequence with total length plus 1 and unchanged sequence length, while a new open sequence of length 1 is initiated, e.g. $O^{a}_{x,y} + B \rightarrow Q^{b}_{x+1,y} + C^{a,b}_{x+1,y}$. The PBE’s describing chain and sequence lengths are solved using a numerical strategy, where the unknown distributions are replaced by linear combinations of Gaussian basis functions with a small number of expansion coefficients. The model is applied to bulk copolymerization of styrene-acrylonitrile in batch, a system with strong composition drift. The 2D-distribution of chain length/B-sequence lengths is shown in Figure 2.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure1}
\caption{Figure 1.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{Figure2}
\caption{Figure 2.}
\end{figure}
Chain Shutting Polymerization ethylene (A) / 1-octene (B).
The reaction scheme of the dual catalyst ethylene/1-octene chain shuttling copolymerization is taken from earlier studies. As shown in Figure 3, Catalyst 1 incorporates both comonomers, yielding the soft blocks and catalyst 2 has a high selectivity for ethylene, yielding hard crystalline blocks. The chain transfer agent is diethyl-zinc, which acts on growing chains at both catalyst sites. In a mono-catalyst system only self-shuttling from and to the same catalyst takes place, in a dual system we may have real cross-shuttling, where a dormant chain from either catalyst site may move to either the same or the other site.

The polymerization system is described by three molecular species: living chains $P_{m,i}^{L}(x, y, z)$, dormant chains $P_{m}^{d}(x, y, z)$, dead chains $P(x, y, z)$, where $x$ is chain length, $y$ is number of A (ethylene) units, $z$ is position of A units in the chain, $m$ is the terminal monomer unit (a, b), and $i$ is catalyst type (1, 2, 3). So, $P_{m,2}(x, y, z)$ denotes the concentration of living chains of length $x$, $y$ A units with a A unit on position $z$, terminating with a B unit, growing on catalyst 2. Note that distinguishing the average positional profiles for chains of a specific length, from 10 to 3000. The dashed lines denote the terminal position, $x = z$.

Initiation from active site $C_i^*$ with A:

$$C_i^* + A \xrightarrow{k_i} P_{a,j}^{L}(1,1,1);$$

A propagation step:

$$P_{a,j}^{r}(x, y, z) + A \xrightarrow{y^{-1}k_{a,j}} P_{a,j}^{r}(x + 1, y + 1, z + 1)$$

The factor $y^{-1}$ corrects for the abovementioned weighting with $y$ inherent to the definition of the concentrations $P$. After solving the associated population balances interesting properties like the average probability of finding an A-unit on position $z$ in chains of length $x$ may be computed:

$$P_A(x, z) = \frac{\sum_{y=1}^{x} y^{-1} P(x, y, z)}{\sum_{z=1}^{x} \sum_{y=1}^{x} y^{-1} P(x, y, z)}.$$

We have performed simulations with this model for a copolymer product of relevant properties, $M_a = 54$ kg/mol, average 1-octene content 10 %, and position, $z$, could be calculated. Figure 4 shows the average positional profiles for chains of a specific length, from 10 to 3000. The dashed lines denote the terminal position, $x = z$.

Conclusions

A new population balance based method has been successfully developed enabling to predict a range of interesting characteristics of copolymers. The bivariate sequence length/chain length distribution for a styrene/acrylonitrile could thus be calculated. For chain shuttling copolymerization of ethylene/1-octene the gradient properties have been obtained.

References