Multisite Model of Polyol Preparation in Continuous Processes Using Heterogeneous Double Metal Cyanide Catalysts

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Abstract

Polyols are typically produced using batch processes and KOH as the dominant homogeneous catalyst. In this case, the main reaction is an ionic polymerization reaction, and products with narrow molecular weight distributions (MWDs) are typically obtained. As observed in living polymerization systems, polyols of varying molecular weights serve as starting points for manufacture of polyols of higher molecular weights.

The transition from batch to continuous processes should lead to polydispersities approaching the theoretical limit of 2 for living polymerization systems. However, with the recent introduction of heterogeneous Double Metal Cyanide (DMC) catalysts, the expected increase in polydispersity is not observed[1]. Polyols produced in continuous processes that use DMC catalysts still have polydispersities approaching 1. This unusual result is the result of a chain-length dependent effect that favors short chains over long chains and thus keeps the molecular weight distribution as narrow as possible, even in continuous reactors. Reaction mechanisms are published that attempt to describe the behavior of DMC catalysts during ring-opening polymerizations[2]. However, these do not go much further than providing a qualitative explanation of the observed results. They also do not address the generation of small fractions of high molecular weight chains[3] observed in the production of polyols with DMC catalysts.

In this paper, we present a model of a backmixed continuous reactor for polyol production using a DMC catalyst. This reactor could be, for example, a mixed flow reactor or a loop reactor with a high recycle ratio[4]. The model considers the propagation reaction to be diffusion-controlled, thus allowing short chains to grow faster in each catalytic site compared to the longer chains and achieving a narrow molecular weight distribution in a single reactor. Furthermore, this model considers that polymerization occurs in two types of active sites with the irreversible conversion of site 1 to site 2, thus allowing the build-up of a distinct population of long chain molecules. The model provides new insight into the system and can be utilized to determine the most appropriate operating conditions for the optimization of final products.

[1] Yamada, K., Takeyasu, H., Ikemura, M., , "Method for continuous preparation of polyethers", Japanese Unexamined Patent Application 6[1994]-16806

[2] Kim, I., Ahn, J., Sik Ha, C., Sik Yang, C., and I. Park, "Polymerization of propylene oxide by using double metal cyanide catalysts and the application to polyurethane elastomer", *Polymer 44*, 3417–3428, 2003

[3] Brons, J. F. J., Eleveld, M. B., "Process for preparing polyoxyalkylene polyether products",EP 1,295,902, 2003

[4] Zacca, J. J., Ray, W. H., "Modeling of the liquid phase polymerization of olefins in loop reactors", Chem. Eng. Sci. 48(22), pp 3743-65, 1993
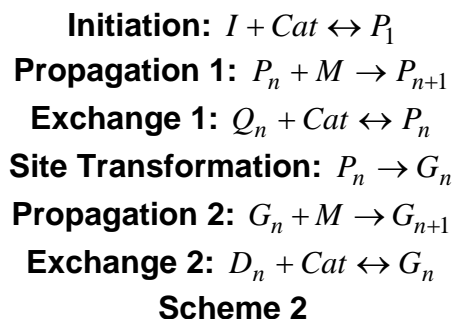
Model Development

Kinetic Scheme

A representative reaction scheme for polyol formation using heterogeneous DMC catalysts that appears in the open literature assumes that only one type of active site exists upon which propagation reaction occurs, as shown in Scheme 1. An active site can be temporally converted into a dormant one through reversible intermolecular chain transfer (or exchange) reaction.

Initiation: $I + Cat \leftrightarrow P_1$

Propagation: $P_n + M \rightarrow P_{n+1}$

Exchange: $Q_n + Cat \leftrightarrow P_n$
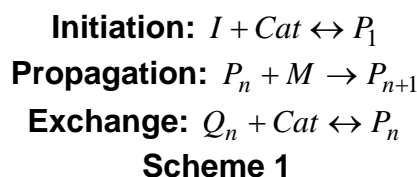
Scheme 1

In Scheme 1, *M* denotes monomer, *I* denotes initiator, *Cat* denotes DMC catalyst, P_n denotes a growing chain with length *n* attached to catalyst, and Q_n denotes a dormant chain with length *n* in solution. P_n can also be considered as a complex between Q_n and *Cat*

A distinct high molecular weight tail in final polyol products using DMC catalysts is observed in both literature and in our own experiments. This suggests that more than two polymer populations exist in the system. In order to have a mechanistic understanding of the experimental observations, in analogy to olefin polymerization using Ziegler-Natta catalysts[5], we believe multiple sites, capable of triggering polymerization, are involved in this system, a logical assumption given the heterogeneous nature of DMC catalysts. For simplicity, we assume that two types of active sites exist in the system. In addition to the reactions in Scheme 1, there are three extra reactions as shown in Scheme 2. Note that we assume that active site of type 2 can only be formed through site transformation reaction from active site of type 1 and the reaction itself is irreversible.

Initiation: $I + Cat \leftrightarrow P_1$

Propagation 1: $P_n + M \rightarrow P_{n+1}$

Exchange 1: $Q_n + Cat \leftrightarrow P_n$

Site Transformation: $P_n \rightarrow G_n$

Propagation 2: $G_n + M \rightarrow G_{n+1}$

Exchange 2: $D_n + Cat \leftrightarrow G_n$

Scheme 2

In Scheme 2, *M* denotes monomer, *I* denotes initiator, *Cat* denotes DMC catalyst, P_n denotes a growing chain of type 1 with length *n* attached to catalyst, Q_n denotes a dormant chain of type 1 with length *n* in solution, G_n denotes a growing chain of type 2 with length *n* attached to catalyst, and G_n a dormant chain of type 2 with length *n* in solution.

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[5] C. M. Chen, Gas Phase Olefin Copolymerization with Ziegler-Natta Catalysts. PhD thesis, University of Wisconsin-Madison, 1993.

Kinetic Model

Based upon Scheme 2, a kinetic model is developed. Note that for simplicity, we treat initiator as dormant polymer chains of type 1 with an initial chain length. The rates of change for all polymer species of interest are written as follows:

- Growing chains of type 1

$$r_{[P_n]} = k_{p1}\left([P_{n-1}] - [P_n]\right)[M] + k_{a1}[Q_n][Cat] - k_{d1}[P_n] - k_{tr}[P_n] \tag{1}$$

- Dormant chains of type 1

$$r_{[Q_n]} = -k_{a1}[Q_n][Cat] + k_{d1}[P_n] \tag{2}$$

- Growing chains of type 2

$$r_{[G_n]} = k_{p2}\left([G_{n-1}] - [G_n]\right)[M] + k_{a2}[D_n][Cat] - k_{d2}[G_n] + k_{tr}[P_n] \tag{3}$$

- Dormant chains of type 2

$$r_{[D_n]} = -k_{a2}[D_n][Cat] + k_{d2}[G_n] \tag{4}$$

where $[A]$ is the concentration of species A

k_{pi} is the propagation rate constant of active site i (i=1,2)

k_{ai} is the activation rate constant of active site i (i=1,2)

k_{di} is the deactivation rate constant of active site i (i=1,2)

k_{tr} is the transformation rate constant from active site 1 to 2

Chain-Length Dependent Rate Constants

Very interesting observations are reported in the patent literature that polyols produced in a CSTR using DMC catalysts show to have narrow MWDs. Normally their polydispersities are close to 1.3. These observations are a distinct contradiction to the conventional wisdom that a living polymerization system operated in a CSTR produces polymers with a polydispersity of 2 due to the broad residence time distributions of the CSTR. To explain such observations, we propose that several reaction steps involved in the system are chain-length dependent. In particular, the shorter chains preferentially grow compared to the longer chains.

In the polymerization of propylene oxide, both propagation and activation of a dormant chain to a growing chain involve a polymer chain and a small molecule. In most modeling studies[6], it is assumed that the migration of small molecules is very fast so that reactions involving a polymer chain and a small molecule are not significantly diffusion-controlled except in the case of high conversion which corresponds to high viscosity. However, most recently when studying pulsed laser polymerization (PLP) followed by size-exclusion chromatograph

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[6] N. A. Dotson, R. Galvan, R. L. Laurence, and M. Tirrell, *Polymerization Process Modeling*, VCH Publishers, Inc. 1996.

(SEC) analysis of chain length distribution (CLD) of the polymers, it is reported that the rate constant of chain propagation k_p in a free radical polymerization system can be chain length dependent. Olaj *et al.*[7] argues that this chain length dependence of propagation rate constant is due to the local accessible monomer concentration to active chain end, which decreases as overall chain length increases. Moreover, they find that the effect is more progressive and salient for short chain lengths compared to longer ones. Even though polymerization of propylene oxide using DMC catalysts does not follow free radical polymerization chemistry, the same argument regarding chain length dependence of propagation can be applied. Moreover, final products in such a system normally have a quite short average chain length; thus, the assumption of chain length dependence rate constant for propagation for this system is reasonable. In the mean time, we can argue that activation of a dormant chain to a growing chain is also chain-length dependent. The activation of a dormant chain involves its absorption to the catalyst surface. It would be much easier for a short chain to be absorbed compared to its longer counterpart. As to deactivation of a growing chain from a catalyst to form a dormant chain, one can use the same argument as activation reaction to claim its chain length dependence. After releasing the catalyst, the dissociated chain and the catalyst are in a zone where either the dissociated chain or the catalyst or both must leave in order to complete the deactivation step. However, these steps are determined by the migration rate of the chain, which is related to chain length.

In this study, we assume that the chain-length dependent reaction rate constant observes the following form:

$$k = k_{01}\left(\frac{1}{n}\right)^{\alpha} + k_{02} \qquad (5)$$

Equation 5 reflects that chain length dependence of a rate constant is most significant for a range of chain lengths. As a chain grows and extends itself long enough, the chain length dependence of a rate constant is less significant. Similar law as shown in Equation 5 for chain length dependent rate constant is used by Nikitin *et al.*[8] in free radical polymerization chemistry.

When investigating kinetic behavior of polymerization of propylene oxide using some DMC catalysts[9] in a batch reactor, it is found that there are two very distinctly different polymerization rate regimes: the first one is very fast and the second one is relatively slow. This difference in polymerization rate regimes can further support the existence of catalyst site transformation. In our experiments in a batch reactor, we found that the transition from the first regime to the second one shows a salient discontinuity, suggesting the nature of catalyst

[7] O. F. Olaj, A. Kornherr, and G. Zifferer, "The influence of chain-length dependent propagation on the evaluation of the chain length dependence of the rate coefficient of bimolecular termination, 1. PLP-SEC methods", Macromol. Theory Simul. 2001, 10, 881-890.
[8] A. N. Nikitin and A. V. Evseev, "Kinetics of free-radical polymerization with chain-length-dependent constants under initiation by laser pulses: effect of chain length dependence of propagation", Macromol. Theory Simul. 1999, 8, 296-308.
[9] C. M. Villa, L. H. Thompson, J. P. Masy, and J. W. Weston, "Complex Dynamic Behavior during Polyol Preparation in Continuous Processes Using Heterogeneous Double Metal Cyanide Catalysts", to be presented at the AIChE meeting in Austin, TX, 2004.

active sites changes. Moreover, it also implies that the site transformation occurs faster when active chain attached with active site 1 becomes longer. In order to reflect this fact, we consider that the chain-length dependence of transformation reaction rate constant from active site 1 to active site 2 observes the following law.

$$k_{tr} = \frac{k_{tr0}}{[1 + \exp(a(n - b))]} \tag{6}$$

in which k_{tr0}, a and b are empirical parameters.

Reactor Model

For the sake of simplicity, we assume that the density of mixture in the reactor does not change. The mass balance equation over the reactor for a species, A (A = P_n, Q_n, M, Cat), of interest can be written as:

$$[A]_f - [A] + r_A \tau = 0 \tag{7}$$

where $[A]_f$ is the concentration of species A in the feed
$\quad$ $[A]$ is the concentration of species A in the reactor
$\quad$ r_A is the generation rate of species A due to reactions
$\quad$ τ is the residence time of the reactor.
Note that in our current modeling work, we are solving balances on all chains since chain lengths are low enough. This is different from the method of moments that aims to solve the leading moments for the purpose of the prediction of polymer average properties. Our model allows for the prediction of the details of the molecular weight distributions.

Results and Discussions

For illustration purposes, we have chosen a catalyst preparation based on literature examples[10] that illustrate well the ability of the two-site model to capture the unique MWD features in such a system. Note that initiator plays a role of initial dormant chains and acts as chain extension seeds upon which final polyol products can be prepared. Figure 1 shows the comparison of GPC plots between experiment and simulation using a two-site model. The polymer has a polydispersity: M_w/M_n = 1.09. As shown in Figure 1, simulation using a two-site model captures well the overall MWD shape and the distinct high molecular weight tail fraction. Figure 2 shows the GPC plots for the overall simulated polymers as well as their deconvoluted polymer fractions from active sites 1 and 2 respectively. Polymer chains from active site 1 constitute the 70% (wt.) low molecular weight fraction while those from active site 2 are the 30% (wt.) high molecular weight fraction. Polymers from active sites 1 and 2 have very narrow MWDs but different mean values (active site 1: M_w/M_n = 1.05; active site 2: M_w/M_n = 1.07), and their blend still has a quite narrow MWD.

[10] Huang, Y., Qi, G., and Y. Wang, "Controlled Ring-Opening Polymerization of Propylene Oxide Catalyzed by Double Metal-Cyanide Complex", *J. Polym. Sci.: Part A: Polym. Chem. 40*, 1142–1150, 2002
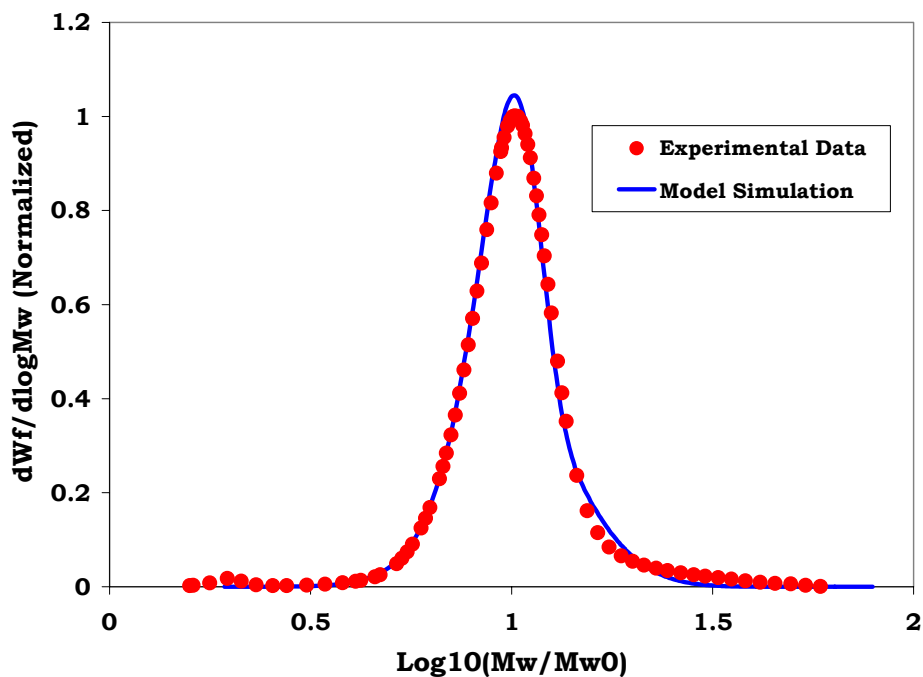
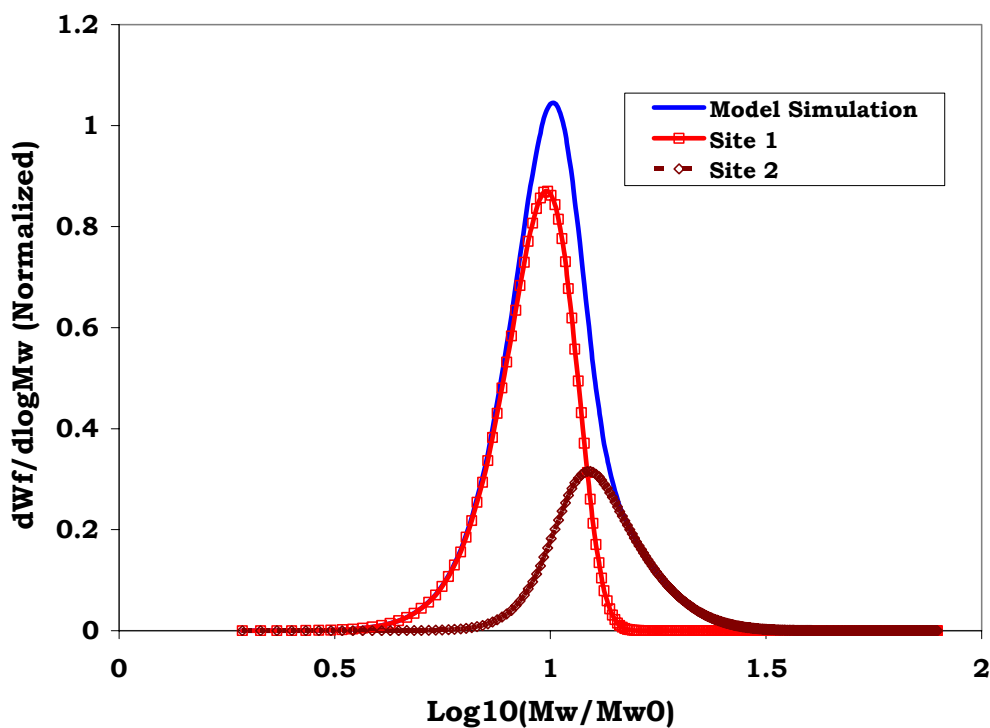**Figure 1. Comparison of GPC plots between experiment and simulation using a two-site model**

Figure 2. GPC plots of overall simulated polymers and their deconvoluted polymer components from active site 1 and 2 respectively

Conclusions

In conclusion, we have successfully developed a model for a single mixed flow reactor by assuming chain length dependent reactions as well as the existence of two types of active sites for the production of polyol using DMC catalysts. The model is capable of explaining the narrow molecular weight distribution of final polyol products and a distinct high molecular weight tail.