

Analysis of Mixed Mode Polymerization Systems. I. Generalized Modeling Approach

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ABSTRACT: Mixed Mode Polymerization (MMP) is introduced and defined as any polymerization process that combines chainwise and stepwise mechanisms, which both contribute to the growth and structure modification of its polymer product. The large difference in activation energies of the growth steps of these two mechanisms provides great flexibility for polymer property control. A large variety of possible combinations including these mechanisms can be designed, which leads to a diversity of processes that require the development of a unified treatment technique. Building on the well-established theories and modeling frameworks available for free-radical polymerization and polycondensation, a generalized approach for modeling MMP is developed. Example applications of the technology are discussed and a case study is analyzed to illustrate the applicability of the generalized modeling approach. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 571–594, 2002

Key words: polymerization; free radical; condensation; modeling

INTRODUCTION

Synthetic polymers occupy a central position in today's industrialized world. For over a century, they were produced by traditional polymerization techniques on the basis of one of the two major mechanisms for polymerization, chainwise or stepwise. Although most polymer production processes adhere strictly to one or the other mechanism, the boundary between the two is beginning to be blurred. In its quest to develop new specialty polymers with specific yet controlled properties, the polymer industry is experimenting with new chemistries as well as combinations of old ones. To meet the ever-increasing quality demands, new techniques such as the use of bifunctional initiators, macromers, and/or reactive additives

are being introduced. Cost concerns, however, restrict the range of possible innovation to the use of traditional monomers and reagents, thus providing the obvious advantage to any process combining proven technologies. In this article, we will consider the broad class of processes that combine chainwise and stepwise polymerization mechanisms, with a special emphasis on predominantly free-radical processes accompanied by varying degrees of condensation. This class of polymerization processes will collectively be referred to as Mixed Mode Polymerization (MMP). According to this definition, the polymerization process involves the simultaneous occurrence of both mechanisms, with the added stipulation that both have to contribute to the growth and structure of the polymer product. Thus, in MMP, the condensation reaction is utilized to provide means of controlling both the microstructure and the molecular weight distribution of the polymer. For example, the large difference in activation energies of

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the growth steps of both mechanisms (the activation energy of condensation is almost twice that of propagation) gives rise to new attractive polymerization pathways and a great flexibility for polymer property control. The focus of this part of the study will be the development of a generalized modeling approach for MMP processes, which is achieved through the analysis of the most common aspects of all processes belonging to this class. Although well-established modeling theories exist for various types of chainwise and stepwise polymerization processes, combinations of both have not yet been treated in a unified manner.

In recent years, there have been cases where the combination of the two types of polymerization was attempted. Even though the resulting polymer products found many applications, the processes that produce them are still under investigation, because they involve many unknown parameters and reaction steps. Most of the applications encountered come from industry and are disclosed in patents. These applications involve one- or two-stage processes and lead to the production of functional polymer backbones. Characteristic examples come from the two-stage production of crosslinkable surface coatings,¹ where an acid or acetoacetoxy functional polymeric material condenses with a nonpolymeric amine functional compound, resulting in high molecular weight product. Other cases come from the production of water-soluble polymers, useful as additives in detergents and cleaning formulations,^{2,3} by reaction of unsaturated dicarboxylic acid monomers with water-soluble monoethylenically unsaturated monomers in the presence of bases. Functionalized polymer formulations have also been developed in a one-stage process by polymerizing ethylenically unsaturated functional monomers, having carboxyl functionalities, with hydroxyl compounds that are attached to the polymer backbone, resulting in polymer products that can be used as builders in detergent compositions, as pigment dispersants in coatings, or as associative thickeners.⁴ Similar cases involve condensation reactions between hydroxyl-substituted hindered amine compounds that can be chemically attached to selected polymer substrates by condensation reactions stabilizing the polymer product⁵ and reactions of functional polymers containing acetoacetate groups with functional amines for polymer products that can be used in coatings, sealants, and adhesives.⁶

The development of functionalized initiators has also contributed in this regard, as these can be used for the production of polymers with reactive terminal functionalities, such as hydroxyl groups.⁷ Even though the technology of functionalized initiator production is still under development, peroxides that contain hydroxyl condensation functionalities have already been produced and were used as crosslinking, grafting, and curing agents, as initiators for polymerization reactions, and as monomers for condensation reactions due to the condensation functionality they contain.⁸⁻¹⁰ The production of monofunctional initiators is already a reality and it is expected that their exploitation in various applications will expand in the near future.

Other applications that provide characteristics similar to MMP are the introduction of terminal and pendant vinyl groups in the polymer chains and the curing of unsaturated polyesters with styrene. The first scenario can be done in polymerization of functional ethylenically unsaturated compounds (containing carboxylic, amino, or alcohol groups) with polycarbodiimides (containing free isocyanate units) to provide polymers with unsaturated groups that can lead to crosslink reactions, resulting in improved polymer properties such as hardness, high elongation, and high-heat distortion temperatures.¹¹ The second scenario leads to crosslink formation because of the reaction of the unsaturated polyester double bonds during the free-radical mechanism, resulting in gel formation. The method is based on a two-stage process where the polyester is first produced via a condensation mechanism and consecutively polymerized with styrene in the presence of a chemical initiator.¹²⁻¹⁶

It is obvious that many polymerization scenarios can be classified as MMP cases. One of the characteristics of this type of polymerization is the presence of various polymer chain structures that complicate the mathematical model development for the investigation of those cases. In addition to that, the combination of two different polymerization philosophies necessitates the introduction of new polymer and monomer unit definitions. The complexity of the mixed mode systems under consideration necessitates the development of a generalized modeling approach that defines and classifies the mixed mode theory. This modeling approach is based on the identification of all the possible states and variables that are needed for the complete description of the polymer molecular weight distribution and its

properties and then to deduce their functional form dependence on the basic reaction steps involved. This relational information is condensed in tabular form that allows for straightforward reduction of the model to suit any specific subsystem in the broad class that is described by MMP. Similar approaches were developed for chainwise¹⁷ and stepwise¹⁸ polymerization systems. Preliminary investigations of specific MMP subsystems and an introduction to the generalized modeling approach were previously presented by the authors.^{19,20,22}

MMP NOMENCLATURE

Any nomenclature system for MMP has to consider three major types of reactive groups: condensation functionalities, polymerizable double bonds, and abstractable chain transfer sites. In polycondensation nomenclature, opposing condensation functionalities are typically symbolized by the capital letters *A* and *B* (e.g., *A* for —COOH and *B* for —OH or —NH₂). In mixed mode systems, however, additional symbols have to be introduced to describe the other reactive group types. The symbols *V* and *T* will be used for vinyl groups and chain transfer sites, respectively. Typical examples of functional vinyl monomers are acrylic acid (CH₂=CH—COOH) and 2-hydroxyethyl methacrylate [HO—CH₂CH₂COO—C(CH₃)=CH₂], which possess a double bond and a condensation functionality each. Based on the symbol definition, these two monomers will be represented as *V*₁*A* and *V*₂*B*, respectively, where the subscripts 1 and 2 are necessary to reflect the identity of the vinyl groups, which could differ markedly in their reactivities. Chain transfer sites (*T*) are usually encountered on a chain transfer agent, but could also be present on any kind of molecule, such as a vinyl monomer (*V-T*) or a condensation reagent (e.g., *A-T*). To complete the nomenclature set, an end group that is considered unreactive will be symbolized by the capital letter *X* (for example, *V-X* indicates a vinyl monomer that can only react by the free-radical mechanism, and *A-X* is a monofunctional condensation reagent).

MMP Example Applications

According to the definition given earlier for mixed mode polymerization systems, numerous and diverse combinations arise. A few of these are detailed here by way of example.

Polymerization in the Presence of Condensation Bifunctional Moieties

This mixed mode case is an example of crosslinking via a condensation mechanism [Fig. 1(a)]. The free-radical mechanism is based on the polymerization of a condensation functional vinyl monomer (*VA*), such as acrylic acid, that produces pendant *A* condensation functionalities in the polymer chains and the crosslinking agent is a molecule that contains two opposite *B* functionalities, such as low molecular weight diols. During polymerization, a variety of polymer structures are formed, such as pendant functionalities of type *A* or *B*, or pendant double bonds. Concurrent production of a new functional monomer *VABB* and a divinyl monomer *VABBAV* is also observed. Condensation reactions between the condensation agent and the opposite functionalities that are provided by the polymer backbone can crosslink the polymer chains, resulting in an increase of the molecular weight of the polymer product.

Copolymerization of Condensation Functional Vinyl Monomers

This case is similar to the previous one in the polymer chain configuration and the obtained crosslink mechanism [Fig. 1(b)]. It is obtained by the copolymerization of two (or more) vinyl monomers containing opposite condensation functionalities (e.g., *V*₁*A*, acrylic acid, and *V*₂*B*, 2-hydroxyethyl methacrylate).

Polymerization in the Presence of Condensation-Monofunctional Moieties

This case can be obtained if polymerization of functional vinyl monomer (*VA*) takes place with the presence of a monofunctional compound that contains opposite *B* condensation functionality [Fig. 1(c)]. This type of polymerization causes modification of the composition and microstructure of the polymer chain, depending on whether the monofunctional material is polymeric or not.

Free-Radical Polymerization Initiated by Condensation Functional Initiators

As previously mentioned, functionalized initiators are available in variations that contain different condensation functionalities. Their use in polymerization leads to the introduction of con-

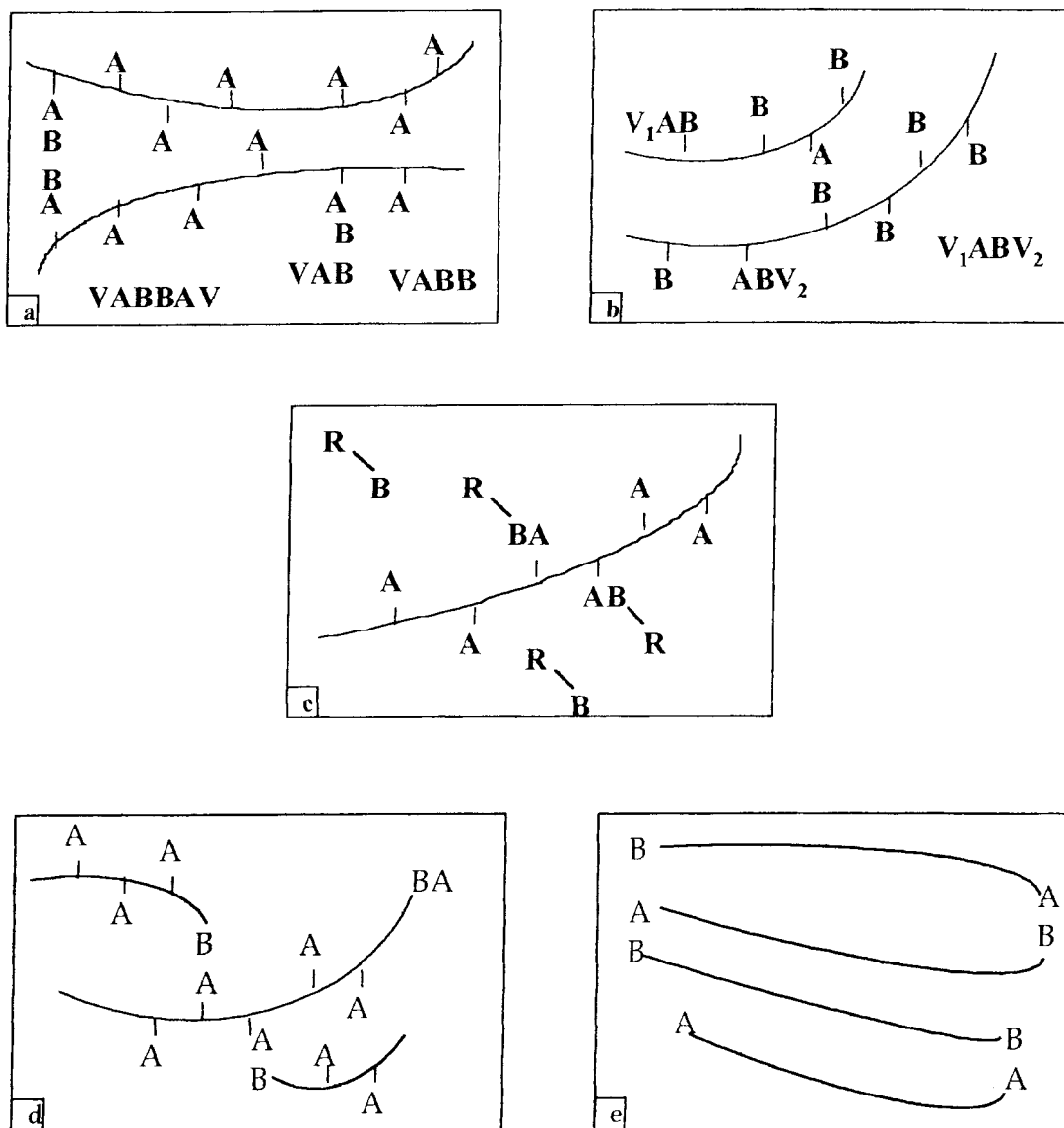


Figure 1 Mixed mode polymerization examples.

densation functionalities at the ends of polymer chains (terminal functionalities). The nature of the initiator, together with its combination with other functional compounds, can result in branch production [polymerization of VA using a BRO-OR'B as initiator, Fig. 1(d)] or simply longer polymer chains [polymerization using ARO-OR'B as initiator, Fig. 1(e)].

Generalized Modeling Approach

The generalized approach was developed to provide a systematic framework for model development, to define and clarify the polymer character-

istics that arise from the combination of the two major modes of polymerization, and to describe all the possible polymerization scenarios that can be classified as mixed mode. The two basic types of polymerization, namely chainwise and stepwise, were extensively investigated in the past from the theoretical point of view. Many specific polymerization models were developed on the basis of the kinetics of the polymerization reactions that occur. Besides the investigation of specific polymerization systems, there were also generalized modeling attempts in cases where various reactants are participating in the reaction mixture. Arriola (1989) developed a generalized modeling ap-

proach for addition polymerization systems¹⁷ to provide a systematic framework that includes many polymerization scenarios. That attempt classified the types of reactions that can take place between various reactants and provided the modeling equations that can be used for the simulation of the polymerization mechanism. This scheme included reactions such as live radical backbiting, beta scission, and chain transfer to polymer. On the other hand, Jacobsen and Ray¹⁸ developed a similar approach for stepwise polymerization. They modeled linear polycondensation processes, considering various mono- and bifunctional condensation monomers that can participate such as *A-A*, *B-B*, *A-B*, *A-X*, and *B-X* species. In addition to the variety of reactant combinations, this modeling approach included several types of possible condensation reactions and the resulting moment equations that lead to the investigation of the polymer molecular weight distribution. Both of these studies^{17,18} have utilized a matrix tabulation technique to relate reactants to specific balance equations, thus considering the model information in an efficient manner. A similar approach will be adopted in this article.

Contrary to the cases of pure chain or step polymerization, the type and number of reactions occurring in any mixed mode polymerization scenario is strongly dependent on the make-up of the system under study. The presence of three kinds of polymerization reactive points (condensation functionalities, double bonds, and transfer sites), as pendant or terminal in the polymer chains, provides a variety of reaction alternatives and products ranging from linear to highly crosslinked polymers. Consequently, one cannot develop a single all-encompassing reaction scheme to describe all possible combinations. Because the number of possible combinations is very large, a major utility of the generalized model is the definition and classification of the mixed mode theory. Furthermore, the structure and composition of the polymer chains and the conditional interactions between various species in the reaction mixture are investigated to represent every polymerization subsystem that can be obtained. Thus, the generalized modeling approach becomes the basis for the derivation of kinetics-based mathematical models for the simulation of a particular mixed mode system and the analysis and optimization of various polymerization processes.

The basic steps of this approach are presented in the next section, followed by an illustrative

application to a specific MMP system. The proposed generalized modeling approach consists of the following successive stages: identification of the reacting species and polymer chain structures, generalized table construction, model reduction and population balance development, state equation, and moment equation development.

To avoid unnecessary mathematical complexities and to provide a clear and comprehensive modeling approach based on the already known types of polymerization basic reactions, two major assumptions had to be made. First, that condensation reactions can only occur between two dead species. This is justified by the large difference in concentration between dead and live polymer chains in a typical free-radical system and by the fact that condensation reactions occur on a time scale much longer than the lifetime of a radical. Relaxation of this assumption would lead to the consideration of polyradicals, which are beyond the scope of our analysis. The second assumption is that all condensation reactions are treated as virtually irreversible. This is a reasonable assumption for a vast proportion of MMP systems, which involve fairly low levels of condensation. Because the level of production of condensate in these systems is low, the rate of the reverse reaction will never be appreciable. In other cases, the assumption of irreversibility will lead to overestimation of the levels of condensation and should be avoided. Because this requires the use of closure techniques that cannot be generalized, we defer their inclusion (which should be straightforward) to the specific application that requires them. One should also note that irreversibility could be forced experimentally by the continuous removal of condensate, which can be achieved by various techniques developed for polycondensation systems.

Identification of the MMP Reacting Species

Four classes of reactants are considered in the MMP framework, namely: initiators, vinyl monomers, condensation agents, and chain transfer agents. Each of these species can possess condensation functionalities and may be mono- or multifunctional. To ensure a background process of free-radical polymerization, it is assumed that any MMP subsystem must comprise at least one initiator and one vinyl monomer in combination with other reagents. Table I summarizes these MMP reacting classes.

Table I MMP Reactant Classes

Initiators	Vinyl Monomers	Condensation Agents	Transfer Agents
RO-OR'	V_nX	AX	AT
ARO-OR'	V_nA	BX	BT
BRO-OR'	V_nB	AA	XT
ARO-OR'A	V_nT	BB	
BRO-OR'B	V_nV_m	AB	
ARO-OR'B			

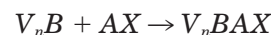
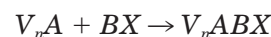
Numerous reactant examples can be given considering the above reactant species such as acrylic acid (V_nA), 2-hydroxyethyl methacrylate (V_nB), styrene (V_nT), vinyl chloride (V_nX), or diethyl acrylate (V_nV_m). Condensation agents containing hydroxyl, amino, or acid functionality can be found in the glycols ($B-B$) and amino acids ($A-B$).

As far as concerns the functionalized initiators, as it was mentioned in the introduction, the production of peroxides with one condensation functionality is already a reality. The types of initiators that are extensively used in free-radical systems are peroxides or azocompounds with one break point that generates two radicals and initiates the polymerization mechanism. In recent years, other types of initiators such as bifunctional initiators were also analyzed.²² Those compounds provide two break points containing two peroxide groups in the same molecule. The rapid developments in initiator technology issues make the goal of production of initiators with two condensation functionalities a possible achievement in the near future.

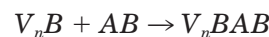
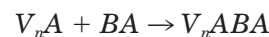
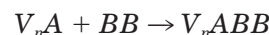
In analyzing MMP systems, it is important to first consider the selection of criteria by which any species present in the system will be classified as either monomeric or polymeric. In free-radical polymerization, polymer is usually defined as any chain (live or dead) of length two or more. In polycondensation, however, the absence of an activation (or initiation) mechanism does not justify the differentiation of monomer molecules from dimers, trimers, and higher polymers. In the treatment of polycondensation, it is customary to lump monomer with high polymer when modeling the molecular weight distribution (MWD) and its averages. The peculiar situation that arises in MMP systems is that condensation reactions can lead to the formation of dimers and trimers that cannot (and should not) be considered as polymeric species. An example is the prod-

uct of condensation of a V_nA monomer with a V_mB monomer, which is a new monomer with two vinyl double bonds (known as a divinyl monomer). To accommodate all of these constraints, MMP terminology considers all species of length two or higher to belong to the polymer population unless exceptions apply. These exceptions occur when a dimer or trimer is formed strictly by condensation and cannot grow further by polycondensation. These species are considered as additional monomers and are considered as such in the model development. Some examples of instances where these monomers occur are presented below.

V_nX Species Formed from Two or Three Monomer Units



V_nA and V_nB Species Formed from Two Monomer Units



V_nV_m Species Formed from Two or Three Monomer Units

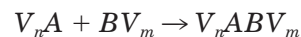
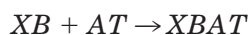
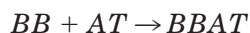
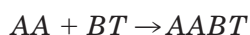


Table II MMP Structural Variables

Entity	Index
Polymer chain length	<i>i</i>
Polymer chain branches	<i>j</i>
Pendant <i>A</i> condensation functionalities in the polymer chains	<i>k</i>
Pendant <i>B</i> condensation functionalities in the polymer chains	<i>l</i>
Pendant double bonds in the polymer chains	<i>m</i>
Pendant transfer sites in the polymer chains	<i>n</i>
Terminal <i>A</i> condensation functionalities in the polymer chains	<i>o</i>
Terminal <i>B</i> condensation functionalities in the polymer chains	<i>p</i>
Terminal double bonds in the polymer chains	<i>q</i>
Terminal transfer sites in the polymer chains	<i>r</i>
Polymer chain crosslinks	<i>s</i>

Transfer Species Formed from Two Monomer Units**Identification of the Polymer Chain Structures**

In a mixed mode environment, the combination of the above reactants results in polymer chains that contain many structures. To describe the polymer chain configuration beyond its chain length, a detailed description of those structures is necessary. These structures can be classified as condensation functionalities, double bonds, and transfer sites. According to their position in the polymer chains, they can be further classified as pendant or terminal.

The reactions that can take place in the MMP environment are initiation (chemical or thermal), propagation, termination (by combination and disproportionation), transfer reactions between live polymer chains and transfer sites, condensation reactions between opposite condensation functionalities, and double bond reactions between live polymer chains and pendant or terminal double bonds in the polymer chains.

The basic characteristic of MMP comes from the added presence of condensation functionalities, which produce polymer structures that affect the molecular weight development. On the basis of the above reaction scheme, pendant condensation functionalities, double bonds, or transfer sites are produced by the free-radical mechanism in cases where functional vinyl monomers, divinyl monomers, or vinyl monomers with trans-

fer sites are used, respectively. Besides these primary free-radical mechanisms, the composition of the already developed pendant structures can be modified by the presence of other active molecules such as condensation and transfer agents that might be present in the same reaction mixture and can be connected with the polymer chains by a condensation mechanism.

On the other hand, the presence of terminal or chain end structures can be obtained with the use of functionalized initiators (for example). The free-radical mechanism is again responsible for the formation of primary condensation functionalities at the ends of the polymer chains. As in the previous case, the identity of those terminal functionalities can be modified by the presence of other condensation functional molecules in the reaction mixture, which might lead to the formation of terminal double bonds or transfer sites.

Additionally, the presence of those chain entities leads to the formation of crosslinks or branch points based on condensation and double bond reactions between pendant and terminal condensation functionalities or double bonds. These new types of branches or crosslinks develop gradually between the polymer chains because they are mostly based on the condensation mechanism, which is usually much slower than that of free-radical propagation.

To describe the configuration of a polymer chain (either dead or live), all the above pendant and terminal structures (together with the chain length) have to be taken into account. These structures will be represented by indices in the polymer chain notation (*P* for dead and *R* for live polymer chains). Table II summarizes all the structural variables together with their index assignments.

Generalized Table Construction

The generalized modeling approach relies on the generation of relational operators among the state variables of the system, which represent the concentrations of the various species as well as the polymeric structures. Two master tables are generated, which provide sufficient information about the polymer development, its configuration, and composition and become the basis for the derivation of the mathematical model for the polymerization process. The relational entries in the cells of the generalized tables are presented in symbolic form for the sake of compactness of information. It is assumed that the translation of these relations could be efficiently generated by skilled personnel or through the use of an expert system that is currently under development in our group. The relations identify production and consumption terms by the use of different symbols (diamonds for production and circles for consumption terms) that are further classified as unconditional or conditional (solid for unconditional and open for conditional terms). The former are terms that appear regardless of the subsystem, whereas the latter necessitates the presence of specific combinations of components in order for them to apply.

The two master tables presented in Tables III–VII represent an all-encompassing reaction scenario. This hypothetical case provides all the possible combinations that can be obtained considering the four sets of reactant groups in the theoretical case where all the reactants that were previously presented are available. The relations are based on the polymerization chemistries that can occur between the reactant species. Each table cell represents a mathematical expression, which is later added as a term in the state equation development. Following the symbol definition, \blacklozenge means production term in the state equation because of the appearance of the corresponding reactant, \bullet is the consumption term, \diamond is the conditional production term (in case of reactant combination), and \circ is the conditional consumption term. In these tables, the primary radicals are indicated with *; the live polymer chains are indicated with the letter *R*, and the dead polymer chains are indicated with the letter *P*. Index definitions for the polymer chains follow the notation of Table II.

The first generalized table (Tables III and IV) provides the state equations (columns) as they are related to the reacting species (rows). The inclusion of the pendant and terminal structures in the

mathematical model development necessitates the construction of a second generalized table (Tables V–VII) that provides information about these quantities considering their relation with the reacting species (the relational symbol definitions are the same as in the first generalized table). The two master tables are the basis for the mathematical model development of any specific mixed mode polymerization case, as is illustrated next.

Model Reduction and Population Balance Development

As mentioned, the two generalized tables contain all the possible mixed mode polymerization scenarios that may occur in the hypothetical case where all types of reactants are present in the same system. Besides their critical importance for the definition and classification of mixed mode polymerization theory, their practical importance is demonstrated in the derivation of a mathematical model for a particular mixed mode case. This constitutes the step of model reduction.

The model reduction technique is defined as the elimination, from the generalized tables, of columns and rows representing species and structures that are not present in the reaction system under investigation. As a result of this procedure, we end up with more compact tables that provide specific information about the development of the population balances of the system under investigation. At this stage, every symbolic relation given in the reduced table cells becomes solid (unconditional) because the system is now fully specified. Notice that some of the conditional terms might drop out if their necessary conditions are not satisfied by the specific subsystem. Summation of the relations over the reduced table columns provides the population balances in terms of production and consumption terms.

State and Moment Equation Development

Translation of the relational terms in the population balances leads to the derivation of the state equations that describe the mixed mode case. Each piece of information that is included in the cells of the reduced table can be translated into a mathematical expression that relates the state variables to the corresponding reacting species. The collection of all expressions in a particular column provides the necessary mathematical model equations that have to be implemented for the simulation of the polymerization reactor.

Table III Generalized Table I (Part 1/2)

	RO*	ARO*	BRO*	$V_r X$	$V_n A$	$V_n B$	$V_n T$	$V_n m$	A-X	B-X
RO*	●			●	●	●	●	●		
ARO*	●			●	●	●	●	●		
BRO*	●			●	●	●	●	●		
$V_n X$	●	●	●	◇ B-X		◇ B-B	◇ B-T	◇ (1) $V_n B$ ◇ (2) B-B		●
$V_n A$	●	●	●			●				
$V_n B$	●	●	●	◇ A-X	◇ A-A		◇ A-T	◇ (1) $V_n A$ ◇ (2) A-A	●	
$V_n T$	●	●	●							
$V_n V_n$	●	●	●							
A-A	●	●	●		◇ $V_n B$ ◇	●		◇ $V_n B$	◇ B-X ◇	●
A-B	●	●	●		◇	◇ $V_n A$		◇ $V_n A$	◇ A-X ◇	●
B-B	●	●	●			◇				●
A-X	●	●	●	◇ $V_n B$				◇ $V_n A$		●
B-X	●	●	●	◇ $V_n A$					◇ A-A	◇ B-B
A-T	●	●	●			●	◇ $V_n B$ ◇ $V_n A$		●	●
B-T	●	●	●						●	
X-T	●	●	●							
$P_{i,j,k,l,m,n,o,p,q,r,s}$	●	●	●	●	◇	◇			◇	◇
$R_{i,j,k,l,m,n,o,p,q,r,s}$	●	●	●	●	◇	◇			◇	◇

● Propagation, transfer reactions
 ◇ Propagation
 ○ Pendant, terminal A
 ○ Pendant, terminal B
 ○ Pendant, terminal A

Table IV Generalized Table I (Part 2/2)

	A-A	A-B	B-B	A-T	B-T	X-T	$P_{i,j,k,l,m,n,o,p,q,r,s}$	$R_{i,j,k,l,m,n,o,p,q,r,s}$
RO*								◆
ARO*								◆
BRO*								◆
$V_n X$								◆
$V_n A$		●	●		●		◇○ Pendant, terminal B	◆● Propagation
$V_n B$	●	●		●			◇○ Pendant, terminal A	◆● Propagation
$V_n T$							◆ Transfer reactions	◆● Propagation, transfer reactions
$V_n V_n$							◇○ Pendant, terminal B	◆● Propagation
A-A	◆◆	◇B-B	◆◆	◇B-T			◇○ Pendant, terminal A/B	
A-B	◆◆	◆◆	◆◆	◆◆	◆◆		◇○ Pendant, terminal A/B	
B-B	●	●	●	●	◇A-T		◇○ Pendant, terminal A	
A-X		◇A-A					◇○ Pendant, terminal B	
B-X	●	●	●	●	●	◇B-T	◇○ Pendant, terminal A	
A-T		●	●	●	●	◇B-X	◇○ Pendant, terminal B	◆● Transfer reactions
B-T	●	●	●	●	◇B-B	◇A-X	◇○ Pendant, terminal A	◆● Transfer reactions
X-T	○	○	○	○	○		◆ Transfer reactions	◆● Transfer reactions
$P_{i,j,k,l,m,n,o,p,q,r,s}$	Pendant, terminal B	Pendant, terminal A	Pendant, terminal B	Pendant, terminal A			◇○ Pendant, terminal A/B	◇○ Double bond, transfer reactions
$R_{i,j,k,l,m,n,o,p,q,r,s}$		A and B					◆ Termination	◆● Propagation
		Transfer reactions	Transfer reactions	Transfer reactions			◇○ Transfer reactions	◆● Double bond, transfer reactions
		Transfer reactions	Transfer reactions	Transfer reactions			○ Double bond reactions	● Termination reactions

Table V Generalized Table II (Part 1/3)

	Pendant A Groups in Polymer Chains	Pendant B Groups in Polymer Chains	Terminal A Groups in Polymer Chains	Terminal B Groups in Polymer Chains
Pendant A groups in dead chains		● (dead chains)		● (dead chains)
Pendant B groups in dead chains	● (dead chains)		● (dead chains)	
Terminal A Groups in dead chains		● (dead chains)		● (dead chains)
Terminal B Groups in dead chains	● (dead chains)		● (dead chains)	
Pendant double bonds in dead chains				
Terminal double bonds in dead chains				
Pendant transfer sites in dead chains				
Terminal transfer sites in dead chains				
RO*	◇ V_nA (live chains)	◇ V_nB (live chains)		
ARO*	◇ V_nA (live chains)	◇ V_nB (live chains)	◆ (live chains)	
BRO*	◇ V_nA (live chains)	◇ V_nB (live chains)		◆ (live chains)
V_nX			◇ ARO* (live chains)	◇ BRO* (live chains)
V_nA	◆ (live chains)	● (dead chains)	◇ ARO* (live chains)	◇ BRO* (live chains)
V_nB	● (dead chains)	◆ (live chains)	◇ ARO* (live chains) ● (dead chains)	◇ BRO* (live chains)
V_nT			◇ ARO* (live chains)	◇ BRO* (live chains)
V_nV_m			◇ ARO* (live chains)	◇ BRO* (live chains)
A-A	◇ Pendant B (dead chains)	● (dead chains)	◇ Terminal B (dead chains)	● (dead chains)
A-B				
B-B	● (dead chains)	◇ Pendant A (dead chains)	● (dead chains)	◇ Terminal A (dead chains)
A-X		● (dead chains)		● (dead chains)
B-X	● (dead chains)		● (dead chains)	
A-T		● (dead chains)		● (dead chains)
B-T	● (dead chains)		● (dead chains)	
X-T				
Live chains	◇ V_nA (live chains)	◇ V_nB (live chains)		

Table VI Generalized Table II (Part 2/3)

	Pendant Double Bonds in Polymer Chains	Terminal Double Bonds in Polymer Chains	Pendant Transfer Sites in Polymer Chains
Pendant A groups in dead chains	$\diamond V_n B$ (dead chains)		$\diamond B-T$ (dead chains)
Pendant B groups in dead chains	$\diamond V_n A$ (dead chains)		$\diamond A-T$ (dead chains)
Terminal A groups in dead chains		$\diamond V_n B$ (dead chains)	
Terminal B groups in dead chains		$\diamond V_n A$ (dead chains)	
Pendant double bonds in dead chains			
Terminal double bonds in dead chains			
Pendant transfer sites in dead chains			
Terminal transfer sites in dead chains			
RO*	$\diamond V_n V_m$ (live chains)		
ARO*	$\diamond V_n V_m$ (live chains)		
BRO*	$\diamond V_n V_m$ (live chains)		
$V_n X$			
$V_n A$	\diamond Pendant B (dead chains)	\diamond Terminal B (dead chains)	
$V_n B$	\diamond Pendant A (dead chains)	\diamond Terminal A (dead chains)	
$V_n T$			\blacklozenge
$V_n V_m$	\diamond Propagation (live chains)		Propagation (live chains)
A-A			
A-B			
B-B			
A-X			
B-X			
A-T			\blacklozenge Pendant B (dead chains)
B-T			\blacklozenge Pendant A (dead chains)
X-T			
Live chains	\diamond Propagation $V_n V_m$ (live chains) \bullet PDB reaction (dead chains)	\bullet Terminal double bond reaction (dead chains)	$\diamond V_n T$ (live chains) \bullet (dead chains)

The full description of the polymer MWD requires the solution of an infinite number of equations because of the length of the polymer chains and the various structures that may appear. The method of moments is a statistical tool that provides a valuable solution to this problem because it reduces the number of equations that have to be solved, but only provides information about the molecular weight distribution in terms of aver-

age-molecular weight values. The method can be applied to the population balance equations developed in the previous stage. Usually, the first three moments are sufficient for the description of the polymer MWD, but summations over multiple indices can lead to a proliferation of higher moments that is not closed. A possible solution for this problem is proposed later in the form of an index reduction technique.

Table VII Generalized Table II (Part 3/3)

	Terminal Transfer Sites in Polymer Chains	Polymer Chain Branches	Polymer Chain Crosslinks
Pendant A groups in dead chains		◇ Terminal B (dead chains)	◇ Pendant B (dead chains)
Pendant B groups in dead chains		◇ Terminal A (dead chains)	◇ Pendant A (dead chains)
Terminal A groups in dead chains	◇ B-T (dead chains)	◇ Pendant B (dead chains)	
Terminal B groups in dead chains	◇ A-T (dead chains)	◇ Pendant A (dead chains)	
Pendant double bonds in dead chains			◆ Live chains (live chains)
Terminal double bonds in dead chains		◆ Live chains (live chains)	
Pendant transfer sites in dead chains		◆ Live chains (live chains)	
Terminal transfer sites in dead chains			
RO*			
ARO*			
BRO*			
$V_n X$			
$V_n A$			
$V_n B$			
$V_n T$			
$V_n V_m$			
A-A			◇ Pendant B (dead chains)
A-B			◇ Pendant A, B (dead chains)
B-B			◇ Pendant A (dead chains)
A-X			
B-X			
A-T	◆ Terminal B (dead chains)		
B-T	◆ Terminal A (dead chains)		
X-T			
Live chains	● (dead chains)	◇ Terminal DB and transfer reactions (live chains)	◇ Pendant DB reactions (live chains)

Illustration of the Modeling Technique

In this section, the case study of polymerization of VA using functionalized initiator BRO-OR'B is used as an illustrative example of an application of the generalized modeling approach to a specific mixed mode case. The system consists of a functional vinyl monomer VA that is polymerized by using a functionalized initiator of type BRO-OR'B. This case, as illustrated in Figure 1(d), represents a mixed mode

nonlinear polymerization scenario that was selected because of the various polymer chain structures that it possesses. This process is considered in a continuous stirred tank reactor (CSTR) of residence time θ .

Application of the Generalized Modeling Approach

The reaction mechanism of the specific case consists of the initiation step which is of critical im-

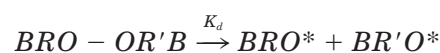
Table VIII VA Polymerization Using Functionalized Initiator (Reduced Table I)

	BRO*	VA	$P_{i,j,k,p,q}$	$R_{i,j,k,p,q}$
BRO*	●	●		◆
VA	●		◆ ● Terminal B	◆ ● Propagation
$P_{i,j,k,p,q}$		● Terminal B	◆ ● Pendant A-Terminal B	◆ ● Terminal double bond
$R_{i,j,k,p,q}$		● Propagation	◆ Termination	◆ ● Propagation, terminal double bond, termination
			● Terminal double bond	

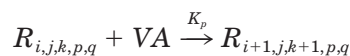
portance because it introduces not only the free radicals in the system but also the condensation functionalities of type *B* at the ends of the polymer chains (terminal). Another type of functionality is that of type *A* that appears as pendant in the polymer chains because of the propagation of the functional vinyl monomer VA. Based on its configuration, the system leads to ternary branch production due to the condensation reactions between the pendant and terminal functionalities. Another characteristic is the appearance of terminal double bonds due to the condensation between terminal *B* functionalities and free-vinyl monomers VA. The appearance of terminal double bonds will lead to terminal double bond propagation, a reaction in which a radical attacks a terminal double bond and produces a ternary branch. Both termination mechanisms (combination and disproportionation) are taken into account, with disproportionation resulting in the

formation of unreactive chain ends. The detailed reaction mechanism for this case study is given by the following:

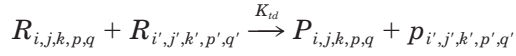
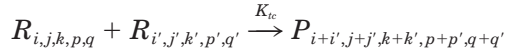
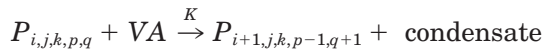
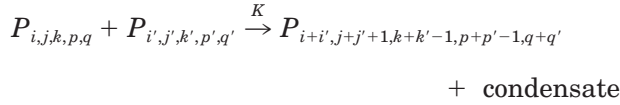
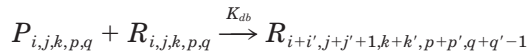
Initiation



Propagation

**Table IX VA Polymerization Using Functionalized Initiator (Reduced Table II)**

	Pendant A Groups in Polymer Chains	Terminal B Groups in Polymer Chains	Terminal Double Bonds in Polymer Chains	Polymer Branches
Pendant A groups		● (dead chains)		◆ Terminal B (dead chains)
Terminal B groups	● (dead chains)		◆ V_nA (dead chains)	◆ Pendant A (dead chains)
Terminal double bonds				◆ Terminal double bond reaction (live chains)
BRO*	◆ VA propagation (live chains)	◆ Initiation (live chains)		
VA	◆ Propagation (live chains)	◆ Initiation (live chains)	◆ Terminal B (dead chains)	
Live chains	◆ VA propagation (live chains)	● (dead chains)	● Terminal double bond reaction (dead chains)	◆ Terminal double bond reaction (live chains)

Termination (combination and disproportionation)

Condensation

Terminal Double Bond Propagation


Thus, the reacting species identified for this system include dead and live polymer chains, free vinyl monomers, and initiator species (or primary radicals). The polymer chain structures to be considered are identified as pendant *A* functionalities (index *k*), terminal *B* functionalities (index *p*), terminal double bonds (index *q*), and ternary branches (index *j*). Model reduction is then carried out by eliminating the rows and columns of the two master tables that do not include these species and structures. The first reduced table (Table VIII) contains information about the population balance equations in terms of production and consumption relations between the state variables (columns) and the reacting species (rows). The second reduced table (Table IX) provides information about the production and consumption of the polymer chain structures and is thus critical for completion of the model equations. The derivation of these equations is enabled by the index reduction technique described later.

The translation of the relational information of the two master tables into mathematical terms requires either knowledge in Polymer Reaction Engineering or the use of tabulated information from an expert database. Figure 2 illustrates this process for the stated equation of the vinyl monomer VA. The symbol in the appropriate cell indicates that this monomer is consumed by reaction with dead polymer chains containing terminal *B*

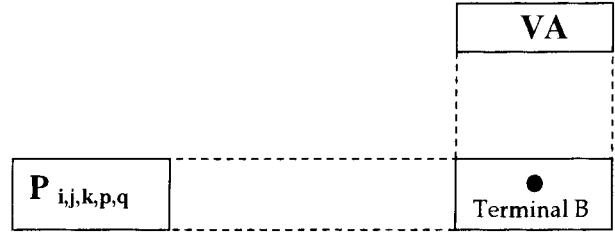


Figure 2 Relation between VA monomer (state) and dead polymer chains.

groups (index *p*). The mathematical expression for this term can thus be obtained as:

$$\frac{dVA}{dt} = \dots - KVA \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} p P_{i,j,k,p,q}$$

The complete state equations that describe the system behavior in terms of concentration units (mol/L) can thus be derived and are presented in what follows.

Dead Polymer Chains

$$\begin{aligned} \frac{dP_{i,j,k,p,q}}{dt} = & \frac{1}{2} K_{tc} \sum_{i'=1}^{i-1} \sum_{j'=0}^j \sum_{k'=1}^{k-1} \sum_{p'=1}^{p-1} \sum_{q'=0}^q \\ & R_{i',j',k',p',q'} R_{i-i',j-j',k-k',p-p',q-q'} \\ & + K_{td} R_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} \\ & R_{i',j',k',p',q'} - Kp P_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} k P_{i',j',k',p',q'} \\ & - Kk P_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} p P_{i',j',k',p',q'} \\ & + K \cdot \sum_{i'=1}^{i-1} \sum_{j'=0}^{j-1} \sum_{k'=1}^{k-1} \sum_{p'=1}^{p-1} \sum_{q'=0}^q \\ & \{ p' P_{i',j',k',p',q'} (k - k' + 1) P_{i-i',j-j'-1,k-k'+1,p-p'+1,q-q'} \\ & - Kp P_{i,j,k,p,q} VA + KVA (p + 1) P_{i-1,j,k,p+1,q-1} \\ & - K_{db} q P_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} R_{i',j',k',p',q'} - \frac{P_{i,j,k,p,q}}{\theta} \end{aligned} \quad (1)$$

Live Polymer Chains (Quasi Steady-State Approximation [QSSA])

$$\begin{aligned}
 \frac{dR_{i,j,k,p,q}}{dt} = & K' BRO^* VA + K'' BRO^* VA \\
 & - K_p VAR_{i,j,k,p,q} + K_p VAR_{i-1,j,k-1,p,q} \\
 & - (K_{tc} + K_{td}) R_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} R_{i',j',k',p',q'} \\
 & + K_{db} \sum_{i'=1}^{i-1} \sum_{j'=0}^{j-1} \sum_{k'=1}^{k-1} \sum_{p'=1}^{p-1} \sum_{q'=0}^q R_{i',j',k',p',q'} (q - q' + 1) P_{i-i',j-j'-1,k-k',p-p',q-q'+1} \\
 & - K_{db} R_{i,j,k,p,q} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} q P_{i',j',k',p',q'} \cong 0
 \end{aligned} \quad (2)$$

Monomer VA

$$\begin{aligned}
 \frac{dVA}{dt} = & - K' BRO^* VA - K'' BR'O^* VA \\
 & - KVAR_{i,j,k,p,q} - KVA \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} p P_{i,j,k,p,q} \\
 & + \frac{VA^{\text{feed}} - VA}{\theta}
 \end{aligned} \quad (3)$$

Initiator (BRO-OR'B)

$$\frac{dI}{dt} = - K_d I + \frac{I^{\text{feed}} - I}{\theta} \quad (4)$$

Primary Radicals (Quasi Steady-State Approximation)

$$\begin{aligned}
 \frac{d(BRO^* + BR'O^*)}{dt} = & 2fK_d I - K' BRO^* VA \\
 & - K'' BR'O^* VA \cong 0
 \end{aligned} \quad (5)$$

Index Reduction Technique

The population balance eqs. (1–2) for live radicals and dead polymer chains involve a total of five indices for the case study at hand. The task of deriving moment equations by summing these

balances over each index independently is burdensome because of the number of multiple moments involved. Furthermore, even if one decided to restrict the model equations to lower moments, an additional problem arises because of the lack of closure of the system of moment equations. Equations for lower moments address higher moments, whose equations address even higher moments. Many methods can be used to resolve this issue, but none is universally accepted. One could resort to the use of moment closure equations which are derived from the assumption of a particular form of the distribution or the use of weighted residual methods which attempt to approximate the distribution with a set of interpolating functions. The situation could, however, be simplified extensively if one could resort to a reasonable technique to reduce the number of indices involved. The methodology we adopt here relies on relating the indices for pendant and terminal structures to one (or both) of two basic indices, namely the index for chain length (i), and that for number of branches (j) or for crosslinks (s), depending on the system. The assumption is that if reasonable composition homogeneity can be expected, the number of pendant groups of a certain type on a chain will depend on its chain length. Situations for which this assumption is valid include the steady state of a CSTR, transients under (or near) azeotropic copolymerization conditions, or batch polymerizations that involve minimal compositional drift. Hence, all pendant structure indices could be expressed to be proportional to the chain length with the constant of proportionality representing the average fraction of pendant functionalities of this type present in the dead (or live) polymer chains, respectively. This is an average quantity that can be easily tracked if one accounted for the change in the total number of pendant groups of this type. Its value is equal to that number divided by the first moment of the polymer chain length distribution. The situation is different, however, for terminal entities because they cannot be related to the size of a chain; for example, one long linear chain might have only one chain end of a specific type, whereas a shorter chain possesses two. Instead, the distribution of terminal groups on the chains will have to depend on the number of chain ends on the polymer molecule. These in turn are easily related to the number of branch points and/or crosslinks. It is straightforward to show that the number of chain ends on any given molecule with

(j) trifunctional branch points and (s) tetrafunctional crosslinks is given by $2 + j + 2s$. Hence, the number of terminal groups of a certain type will be proportional to this value, with a proportionality constant equal to the average fraction of terminal functionalities for the entire polymer population. This average is equal to the total number divided by the total number of chain ends (which can be related to the zeroth moment on branches). The approximation for pendant entities works well under most circumstances; however, that for terminal ones only works if either termination is predominantly by a bimolecular mechanism, or crosslinking dominates over trifunctional branching. A more robust approach for terminal group estimation is developed in the appendix, and the validity of both approximations is discussed. In all cases, the reduction of the number of necessary indices down to two (or three) proves to be invaluable for the process of derivation of the moment equations. For the case under study, the applied transformations for pendant A, terminal B, and terminal double bonds are mathematically expressed, respectively, as:

$$k = \tilde{k}i \quad (6)$$

$$p = \tilde{p}(2 + j) \quad (7)$$

$$q = \tilde{q}(2 + j) \quad (8)$$

where \tilde{k} , \tilde{p} , and \tilde{q} are the average fractions of these structures in the dead polymer chains. On the basis of the above transformations, the equations for the polymer populations are transformed into the following form:

Dead Polymer Chains

$$\begin{aligned} \frac{dP_{i,j}}{dt} = & \frac{1}{2} \cdot K_{tc} \sum_{i'=1}^{i-1} \sum_{j'=0}^j R_{i',j'} \cdot R_{i-i',j-j'} \\ & + K_{td} \cdot R_{i,j} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} R_{i',j'} - K \cdot \tilde{p}(2 + j) \\ & \times P_{i,j} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \tilde{k}i' \cdot P_{i',j'} - K \cdot \tilde{k}i \end{aligned}$$

$$\begin{aligned} & \times P_{i,j} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \tilde{p}(2 + j') \cdot P_{i',j'} \\ & + K \sum_{i'=1}^{i-1} \sum_{j'=0}^{j-1} \tilde{p}(2 + j') \cdot P_{i',j'} [\tilde{k}(i - i') + 1] \\ & \times P_{i-i',j-j'-1} - K \cdot \tilde{p}(2 + j) \cdot P_{i,j} \cdot VA + K \cdot VA \\ & \times [\tilde{p}(2 + j) + 1] \cdot P_{i-1,j} \\ & - K_{db} \cdot \tilde{q}(2 + j) \cdot P_{i,j} \cdot \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} R_{i',j'} - \frac{P_{i,j}}{\theta} \quad (9) \end{aligned}$$

Live Polymer Chains

$$\begin{aligned} \frac{dR_{i,j}}{dt} = & K' BRO^*VA + K'' BR'O^*VA - K_p VAR_{i,j} \\ & + K_p VAR_{i-1,j} - (K_{tc} + K_{td})R_{i,j} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} R_{i',j'} \\ & + K_{db} \cdot \sum_{i'=1}^{i-1} \sum_{j'=0}^{j-1} R_{i',j'} \tilde{q}(2 + j - j' - 1) P_{i-i',j-j'-1} \\ & - K_{db} R_{i,j} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \tilde{q}(2 + j') P_{i',j'} \cong 0 \quad (10) \end{aligned}$$

As mentioned, the average quantities introduced will be calculated by individual equations that can be derived on the basis of the second reduced table (Table IX) that provides all the necessary information about the overall balances of these structures in the polymer chains. These equations are given below.

Overall Pendant A Functionalities in Dead Chains c_k and Average Fraction \tilde{k}

$$\frac{dc_k}{dt} = 2fK_d I + K_p VA \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} R_{i,j} - Kc_k c_p - \frac{c_k}{\theta} \quad (11)$$

$$\tilde{k} = \frac{c_k}{\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} iP_{i,j}} \quad (12)$$

Overall Terminal B Functionalities in Dead Chains c_p and Average Fraction \tilde{p}

$$\frac{dc_p}{dt} = 2fK_dI - Kc_kc_p - KVAc_p - \frac{c_p}{\theta} \quad (13)$$

$$\tilde{p} = \frac{c_p}{\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} (2+j)P_{i,j}} \quad (14)$$

Overall Terminal Double Bonds in Dead Chains c_q and Average Fraction \tilde{q}

$$\frac{dc_q}{dt} = KVAc_p - K_{db}c_q \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} R_{i,j} - \frac{c_q}{\theta} \quad (15)$$

$$\tilde{q} = \frac{c_q}{\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} (2+j)P_{i,j}} \quad (16)$$

The above set of eqs. (9–16) together with the equations for the monomer and initiator species (3–5) constitute the mathematical model that will be used for the simulation of the case study. The last step of the generalized approach is the development of the moment equations, which given eqs. (9–10) could alternately be generated by an automated expert system. The moments will be applied on two indices such as the chain length and the number of branches in a polymer chain. The resulting moment equations are as follows:

Dead Polymer Moments

$$\begin{aligned} \frac{dQ_{0,0}}{dt} = & \left(\frac{1}{2}K_{tc} + K_{td} \right) (Y_{0,0})^2 + K_{td}(Y_{0,0})^2 \\ & - K\tilde{k}\tilde{p}Q_{1,0}(2Q_{0,0} + Q_{0,1}) \\ & - K_{db}\tilde{q}Y_{0,0}(2Q_{0,0} + Q_{0,1}) - \frac{Q_{0,0}}{\theta} \quad (17) \end{aligned}$$

$$\begin{aligned} \frac{dQ_{1,0}}{dt} = & (K_{tc} + K_{td})Y_{0,0}Y_{1,0} + KVA\tilde{p}(2Q_{0,0} + Q_{0,1}) \\ & - K_{db}Y_{0,0}\tilde{q}(2Q_{1,0} + Q_{1,1}) - \frac{Q_{1,0}}{\theta} \quad (18) \end{aligned}$$

$$\begin{aligned} \frac{dQ_{2,0}}{dt} = & K'BRO*VA + K''BR'O*VA \\ & + 2K_pVAY_{1,0} + K_pVAY_{0,0} + K_{tc}(Y_{1,0})^2 \\ & + K\tilde{k}\tilde{p}(4Q_{1,0}Q_{2,0} + 2Q_{2,0}Q_{1,1}) \\ & + KVA\tilde{p}(2Q_{0,0} + 4Q_{1,0} + Q_{0,1} + 2Q_{1,1}) \\ & + K_{db}\tilde{q}(2Q_{1,1}Y_{1,0} + 4Q_{1,0}Y_{1,0}) - \frac{Q_{2,0}}{\theta} \quad (19) \end{aligned}$$

$$\begin{aligned} \frac{dQ_{0,1}}{dt} = & (K_{tc} + K_{td})Y_{0,0}Y_{0,1} + K\tilde{k}\tilde{p}(2Q_{1,0}Q_{0,0} \\ & + Q_{1,0}Q_{0,1}) - K_{db}Y_{0,0}\tilde{q}(2Q_{0,1} + Q_{0,2}) - \frac{Q_{0,1}}{\theta} \quad (20) \end{aligned}$$

$$\begin{aligned} \frac{dQ_{0,2}}{dt} = & K'BRO*VA + K''BR'O*VA \\ & + 2K_{tc}Y_{0,1}Y_{0,0} + K_{td}Y_{0,2}Y_{0,0} + K\tilde{k}\tilde{p}(2Q_{1,0}Q_{0,0} \\ & + 2Q_{1,0}Q_{0,2} + 4Q_{1,0}Q_{0,1} + 4Q_{1,1}Q_{0,0} + 4Q_{1,1}Q_{0,1} \\ & + Q_{1,0}Q_{0,1} + 2Q_{1,1}Q_{0,1} + 2Q_{1,1}Q_{0,2}) + K_{db}\tilde{q}(Y_{0,0}Q_{0,1} \\ & + 2Y_{0,1}Q_{0,1} + 2Y_{0,1}Q_{0,2} + 2Y_{0,0}Q_{0,0} + 2Y_{0,0}Q_{0,2} \\ & + 4Y_{0,1}Q_{0,0} + 4Y_{0,0}Q_{0,1} + 2Y_{0,1}Q_{0,1}) - \frac{Q_{0,2}}{\theta} \quad (21) \end{aligned}$$

$$\begin{aligned} \frac{dQ_{1,1}}{dt} = & K'BRO*VA + K''BR'O*VA + K_pVAY_{0,1} \\ & + K_{tc}Y_{1,0}Y_{0,1} + K\tilde{k}\tilde{p}(2Q_{2,0}Q_{0,1} + 2Q_{2,0}Q_{0,0} \\ & + 2Q_{1,0}Q_{1,0} + 2Q_{1,1}Q_{1,0} + Q_{2,0}Q_{0,2} + Q_{2,0}Q_{0,1} \\ & + Q_{1,0}Q_{1,1} + Q_{1,1}Q_{1,1}) + KVA\tilde{p}(2Q_{0,1} + Q_{0,2}) \\ & + K_{db}\tilde{q}(2Y_{1,0}Q_{0,0} + Y_{1,0}Q_{0,1} + 2Y_{1,0}Q_{0,1} \\ & + 2Y_{1,0}Q_{0,2} + 2Y_{0,0}Q_{1,0} + Y_{0,0}Q_{1,1} \\ & + 2Y_{0,1}Q_{1,0} + Y_{0,1}Q_{1,1}) - \frac{Q_{1,1}}{\theta} \quad (22) \end{aligned}$$

Live Polymer Moments

$$Y_{0,0} = \sqrt{\frac{2fK_dI}{(K_{tc} + K_{td})}} \quad (23)$$

$$Y_{1,0} = \frac{2fK_dI + K_pVAY_{0,0} + K_{db}\tilde{q}Y_{0,0}(2Q_{1,0} + Q_{1,1})}{(K_{tc} + K_{td})Y_{0,0}} \quad (24)$$

$$Y_{2,0} = \frac{\begin{cases} 2fK_d I + 2K_p V A Y_{1,0} + K_p V A Y_{0,0} \\ + K_{ab} \tilde{q} Y_{0,0} (2Q_{2,0} + Q_{2,1}) \\ + K_{ab} \tilde{q} Y_{1,0} (4Q_{1,0} + 2Q_{1,1}) \end{cases}}{(K_{tc} + K_{td}) Y_{0,0}} \quad (25)$$

$$Y_{0,1} = \frac{2fK_d I + K_{ab} \tilde{q} Y_{0,0} \times (2Q_{0,0} + Q_{0,1} + 2Q_{0,1} + Q_{0,2})}{(K_{tc} + K_{td}) Y_{0,0}} \quad (26)$$

In the above equations, closure problems have appeared in the development of the $Q_{2,0}$, $Q_{1,1}$, and $Q_{0,2}$ moments. However, the use of the QSSA enables us to substitute for the live moments $Y_{2,0}$, $Y_{1,1}$, and $Y_{0,2}$ into their equations, which leads to the elimination of this closure problem.

Monomer VA

$$\frac{dVA}{dt} = -2fK_d I - K_p Y_{0,0} VA + K_2 VA \tilde{p} (2Q_{0,0} + Q_{0,1}) + \frac{VA^{\text{feed}} - VA}{\theta} \quad (27)$$

Initiator

$$\frac{dI}{dt} = -K_d I + \frac{I^{\text{feed}} - I}{\theta} \quad (28)$$

Pendant and Terminal Functionalities

$$\frac{dc_k}{dt} = 2fK_d I + K_p V A Y_{0,0} - K \tilde{k} Q_{1,0} \tilde{p} (2Q_{0,0} + Q_{0,1}) - \frac{\tilde{k} Q_{1,0}}{\theta} \quad (29)$$

$$\frac{dc_p}{dt} = 2fK_d I - K \tilde{k} Q_{1,0} \tilde{p} (2Q_{0,0} + Q_{0,1}) - K V A \tilde{p} (2Q_{0,0} + Q_{0,1}) - \frac{\tilde{p} (2Q_{0,0} + Q_{0,1})}{\theta} \quad (30)$$

$$\frac{dc_q}{dt} = K V A \tilde{p} (2Q_{0,0} + Q_{0,1}) - K_{ab} \tilde{q} (2Q_{0,0} + Q_{0,1}) Y_{0,0} - \frac{\tilde{q} (2Q_{0,0} + Q_{0,1})}{\theta} \quad (31)$$

The above mathematical expressions (17–31) represent the model equations when the method of

moments and the proposed index reduction technique are used.

Direct Model Solution

To assess the validity of the index reduction technique, we chose to compare the steady-state results of the model to those obtained by the direct solution method. Direct model solution is the analytical solution of the model eqs. (1–5) for all possible polymer chain combinations. This is applied for a CSTR at steady state, to avoid the necessity of solving a very large number of coupled ordinary differential equations. The advantage of this method is that it provides the exact populations for all the chain configurations of the polymer system. The disadvantage is that it requires the solution of a very large number of equations resulting in computer memory limitation problems. The equations used for the direct solution method are included in the appendix.

The validation of the index reduction technique was made by comparison between the modified method of moments and the direct solution at steady-state CSTR operation for constant residence time and different reaction temperatures. The primary quantities that are compared are the resulting chain length moments (zero, first, and second) with the equivalent summations that are calculated from the direct solution. Additional averages are also compared and presented in Table X. Theoretically, summations on all indices have an upper limit of ∞ . Our calculations are based on substituting a suitable upper bound for each index, such that the convergence of the summation in question is insured.

Figures 3–6 present a set of steady-state results obtained for the case study under consideration when the polymerization is conducted in a CSTR. These figures illustrate the effect of the steady-state reactor temperature on the dead polymer moments and the polymer branching density. Because the moments are used to calculate the molecular weight averages, the effect of temperature on these can also be deduced. The impact of the condensation mechanism, which leads to ternary branching by the reaction of pendant A groups with terminal B groups, is evident in the behavior of the moments. For example, Figure 3 shows a decrease in Q_0 after about 460 K, which is attributable to an increase in the condensation reaction rate, which leads to a decrease in the number of polymer chains while forming ternary branch points. This effect is also

Table X Equivalence Between Moments/Averages and Direct Summations

Moment or Average Quantity	Direct Solution Equivalent Summation
$Q_{0,0}$	$\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} P_{i,j,k,p,q}$
$Q_{1,0}$	$\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} i \cdot P_{i,j,k,p,q}$
$Q_{2,0}$	$\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} i^2 P_{i,j,k,p,q}$
Branching density: $\frac{Q_{0,1}}{Q_{1,0}}$	$\frac{\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} j P_{i,j,k,p,q}}{\sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} i P_{i,j,k,p,q}}$
\bar{p} (for a given j)	$\frac{\sum_{i=1}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} p P_{i,j,k,p,q}}{2 \sum_{i=1}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} P_{i,j,k,p,q} + j \sum_{i=1}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} P_{i,j,k,p,q}}$

evident in the steady increase in branching density of the polymer product as the reactor temperature increases (Fig. 6). These figures also include a comparison of the model results to those obtained by the direct solution method. The agreement between the two methods is remarkable and seems to indicate the validity of the index-reduction technique used to resolve the moment closure and proliferation problem. Further scrutiny, however, shows that this good agreement can only be attributed to the approximation used for the pendant group indices and not for the terminal group indices. Because of the low level of branching encountered in this system, the calculation of the

chain length moments and of any pendant entity (such as the branching density of Fig. 6) will not be strongly affected by errors in the calculation of terminal entities. The effect on terminal characteristics is, however, very large, as seen in Figure 7. In this figure, the fraction of terminal groups that are of type *B* is plotted against the number of branches on the polymer chain. According to the index reduction technique used in the model, this fraction should be independent of the number of branches on the chain, as it assumes that the chain ends are uniformly distributed. Figure 7, however, reflects a steady decrease in this fraction as a function of the number of branches. It is

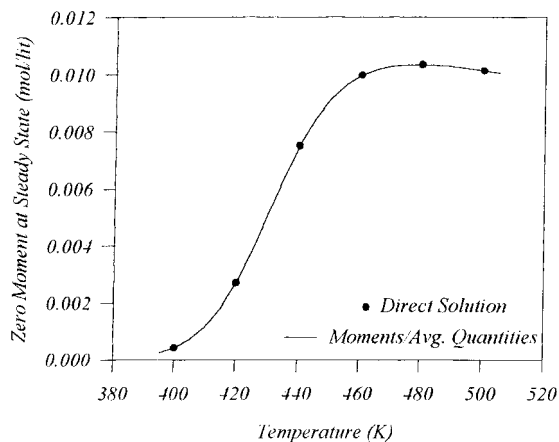


Figure 3 Zeroth moment (SS) versus temperature.

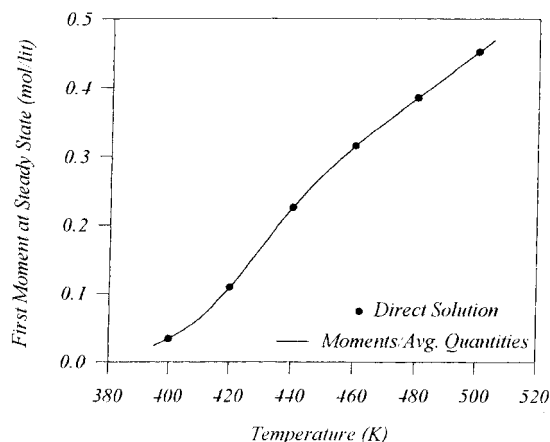


Figure 4 First moment (SS) versus temperature.

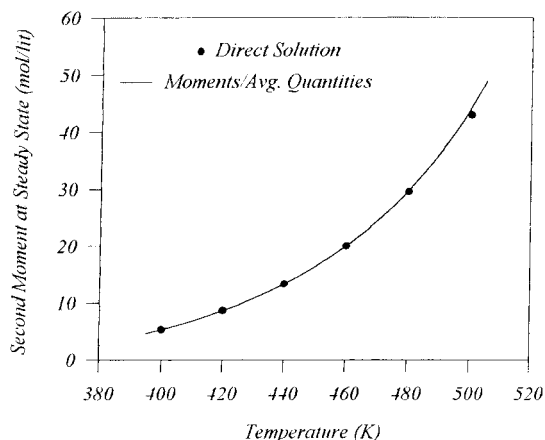


Figure 5 Second moment (SS) versus temperature.

clear then that whether terminal groups are uniformly distributed or not depends strongly on the reaction mechanism. This behavior is analyzed in the appendix, where an alternate index reduction technique is also proposed for use whenever uniformity is not achieved.

CONCLUSION

Mixed mode polymerization is introduced in this article as a polymerization technology that combines aspects from chainwise and stepwise mechanisms. A vast number of processes can be classified as belonging to the MMP class, creating a diversity of systems that defies description under a unified theory. This challenge was resolved, however, by focusing on the essential common

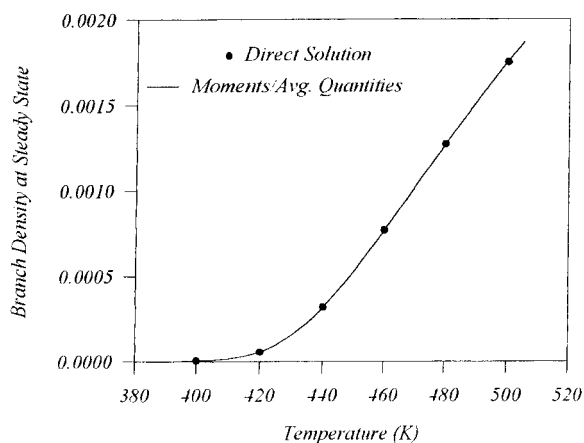


Figure 6 Branching density (SS) versus temperature.

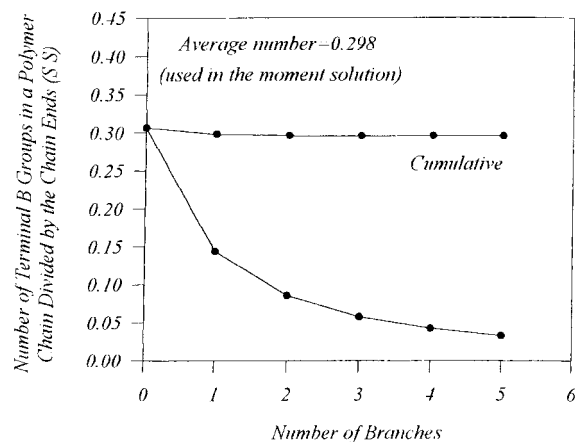


Figure 7 Branch distribution of terminal *B* groups at 480 K, direct solution.

features that repeatedly arise in these systems. A generalized modeling approach is proposed in this article and consists of the steps of (a) Identification of reacting species; (b) Identification of polymer chain structures; (c) Generalized table construction; (d) Model reduction; and (e) Model development. The information generated by this approach is presented in a compact tabular form that requires a familiarity with polymerization modeling principles to develop a mathematical model for a specific MMP application. This translation process is, however, amenable to automation and can be programmed through the use of an expert symbolic database.

The models generated can be derived in any of different levels of complexity depending on the needs of the specific application. A method for approximating higher moments through the use of index reduction is proposed and found to simplify model development efforts. The technique was found to perform adequately as compared to the direct solution method for an example case study, but exceptions to its widespread use have been identified. A refinement of this technique is presented in the appendix, but needs only be used when necessitated by the polymerization chemistry.

Subsequent parts of this series will present theoretical and experimental investigations of specific MMP systems and will explore the range of utility of this technology for the control and modification of polymer properties and microstructure.

APPENDIX

The index reduction technique proposed in the text involves assumptions for the distribution of

pendant and terminal chain structures. The approximation for pendant structure holds whenever a fairly homogeneous composition can be expected in the polymer chain, which is applicable to a wide range of polymerization conditions. Systems that experience severe compositional drifts cannot be treated in the same manner and will either require the solution of the complete moments set or the discretization of the polymer population in a second independent direction (such as birth time) into lumps expected to maintain reasonable compositional homogeneity. In general, the pendant entity approximation was found to perform adequately.

On the other hand, to approximate terminal structures, it was assumed that chain ends are uniformly distributed. Although this assumption is valid for some conditions, it can lead to severe deviations from reality for other conditions, as was illustrated in Figure 7. In general, systems that involve strict bimolecular termination and where only quaternary branching (i.e., crosslinking) occurs will exhibit a uniform distribution of chain end types. This is a result of the fact that no chain ends are created during termination by combination and that no chain ends are consumed by the crosslinking mechanism (unlike ternary branching). It is expected thus that unimolecular termination reactions (disproportionation, chain transfer, or chain scission), especially in ternary branching systems, will lead to deviations from the total homogeneity of the chain end distribution. Modification of the technique for these cases is attempted in this appendix.

In the case study considered, the concentration of terminal groups of type B is given by eq. (7). Let us rewrite it in terms of $\alpha(B)$, the probability that a chain end will be of this type:

$$p = \alpha(B)(2 + j) \quad (\text{A.1})$$

We have assumed that this probability is constant and independent of both chain length and number of branches on the chain. To understand deviations from this assumption, let us consider a system where initiation produces terminal B , where ternary branching occurs via condensation with pendant A and where termination is strictly by disproportionation. Without loss of generality, let us neglect the direct condensation reaction between monomer and terminal B , which would lead to the production of reactive terminal double bonds. Each polymer chain in this system, regardless of how branched it is, will have exactly one

terminal B and all other chain ends will be of type X , the unreactive group produced by the termination reaction. Hence, the fraction of B chain ends decreases as the number of branches increases.

To correct for this effect, we must consider the primary chains that make up any polymer molecule. Out of the primary chains on a given molecule, only one will have two free ends (i.e., does not start at a branch point). This type of chain will be referred to as the main primary chain of the polymer molecule. This situation is, of course, not strictly valid for cases with quaternary branching, but there always exists a topological transformation that allows the remapping of the chain into that structure by assuming that each quaternary branch point consists of two ternary branch points. It is obvious that the distribution of chain ends for the main primary chains will be different from that for the rest, which all must have at least one end at a branch point. Hence, the source of deviation from chain end homogeneity. Under this scenario, eq. (A.1) should be modified to:

$$p = 2\alpha_1(B) + j\alpha_2(B) \quad (\text{A.2})$$

where $\alpha_1(B)$ is the probability that a chain end on a main primary chain is of type B , whereas $\alpha_2(B)$ is the probability that a ternary branch point leads to a chain end of this type. These two probabilities have to be calculated independently and then used in the index reduction technique. Note that in cases where termination is strictly by combination or the only branching mechanism involves crosslinking, these probabilities are equal and eq. (A.2) reduces to (A.1).

To illustrate the calculation of these new probabilities, let us reconsider the case of Figures 3–7. If in this system termination is solely by combination, then all chain ends will either have a B or a reactive double bond V . Furthermore, the distribution of these types will be uniform because it only depends on the condensation reaction between monomer and terminal B , which has the same probability for all unreacted B groups. In this case,

$$\alpha_1(B) = \alpha_2(B) = \frac{c_p}{c_p + c_q} \quad (\text{A.3})$$

and will remain independent of the branching level of the polymer chain. Notice that c_p and c_q are given by eqs. (13) and (15). On the other hand, if termination is strictly by disproportionation, then $\alpha_1(X) = 1/2$ and $\alpha_2(X) = 1$, because each main primary chain will have exactly one (of two)

chain end of type X and because each branch point must lead to a terminal X . Consequently, we can calculate the probabilities for terminal B as follows:

$$\alpha_1(B) = \frac{1}{2} \left(\frac{c_p}{c_p + c_q} \right), \quad \alpha_2(B) = 0 \quad (\text{A.4})$$

As a result, p the number of terminal B groups on a chain is the same for all chains, but the fraction of chain ends that is of this type will be a function of the number of branches on the chain as given by:

$$\tilde{p} = \frac{\left(\frac{c_p}{c_p + c_q} \right)}{2 + j} \quad (\text{A.5})$$

Dead polymer chains

$$\begin{aligned}
 P_{i,j,k,p,q} = & \frac{\frac{1}{2} k_{tc} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} R_{i-i',j-j',k-k',p-p',q-q'} R_{i',j',k',p',q'} \\
 & + k_{td} R_{i,j,k,p,q} \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} R_{i,j,k,p,q} + K \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} \\
 & \{(k - k' + 1) P_{i-i',j-j'-1,k-k'+1,p-p'+1,q-q'} P'_{i',j',k',p',q'}\} \\
 & + KVA \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} (p + 1) P_{i-1,j,k,p+1,q-1} \\
 & \frac{Kk \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} p P_{i,j,k,p,q} + Kp \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} k P_{i,j,k,p,q} \\
 & + KpVA + K_{db}q \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} R_{i,j,k,p,q} + \frac{1}{\theta}}
 \end{aligned} \quad (\text{A.6})$$

Live polymer chains

$$\begin{aligned}
 R_{i,j,k,p,q} = & \frac{2fK_d I + K_p VA R_{i-1,j,k-1,p,q} \\
 & + K_{db} \sum_{i'=1}^{\infty} \sum_{j'=0}^{\infty} \sum_{k'=1}^{\infty} \sum_{p'=1}^{\infty} \sum_{q'=0}^{\infty} (q - q' + 1) \\
 & P_{i-i',j-j'-1,k-k',p-p',q-q'+1} \cdot R_{i',j',k',p',q'}}{K_p VA + K_{tc} \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} R_{i,j,k,p,q} \\
 & + K_{td} \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} R_{i,j,k,p,q} \\
 & + K_{db} \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} q P_{i,j,k,p,q}}
 \end{aligned} \quad (\text{A.7})$$

Figure A.1 presents a plot of this relation for different values of $c_p/(c_p + c_q)$ and provides an explanation for the behavior demonstrated in Figure 7, in which termination was predominantly by disproportionation. In cases where the termination mechanism is mixed, the calculation of probabilities is a little more involved, but should still be tractable.

The Direct Solution method involves the solution of the model equations given by (1–5) for a CSTR at steady state. The resulting model consists of explicit algebraic equations that are to be evaluated for all reasonable values of all five indices included in the case study. These equations are given by the following.

Vinyl monomer VA

$$\begin{aligned}
 VA & \\
 & = \frac{VA^{\text{feed}}}{\theta} \\
 & \frac{2fK_d I + K_p R_{i,j,k,p,q} + K \sum_{i=1}^{\infty} \sum_{j=0}^{\infty} \sum_{k=1}^{\infty} \sum_{p=1}^{\infty} \sum_{q=0}^{\infty} p P_{i,j,k,p,q} + \frac{1}{\theta}}
 \end{aligned} \quad (\text{A.8})$$

Initiator

$$I = \frac{I^{\text{feed}}}{K_d + \frac{1}{\theta}} \quad (\text{A.9})$$

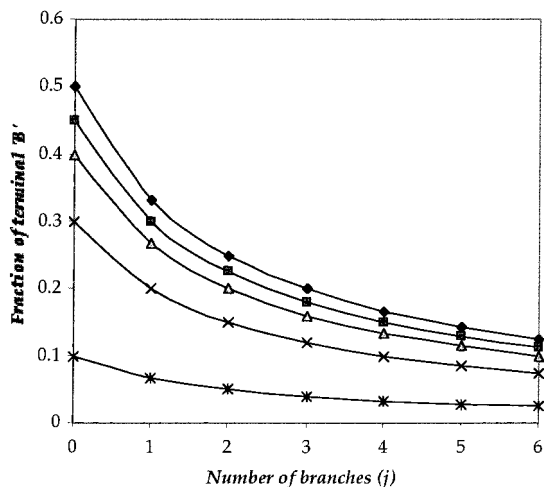


Figure A.1 Modified index reduction results for \bar{p} , for termination by disproportionation. The value of $c_p/(c_p + c_q)$, from top to bottom, is 1.0, 0.9, 0.8, 0.6, and 0.2, respectively.

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