Polymer 126 (2017) 74–86

Contents lists available at ScienceDirect

Polymer

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

Modeling of the polymerization of linear monomers in the presence of multifunctional units

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ARTICLE INFO

Article history:
Received 4 June 2017
Received in revised form
4 August 2017
Accepted 5 August 2017
Available online 9 August 2017

Keywords:
Multifunctional unit
Branched polymer
Molecular weight distribution

ABSTRACT

A rigorous model is developed to predict the configurations of the branched polymers formed by the copolymerization of linear monomers in the presence of multifunctional branching units. Conventional studies on the configuration of branched polymers generally consider the statistical properties of the growth of only one element or polymerization from one component (e.g., dendrimers, hyperbranched, and hypergrafted polymers from AB*m* or ABC-type monomers). This study considers combinations of several types of linear and branched elements and the simultaneous aggregation of branched element-branched element and monomer-monomer elements. The proposed method is based on a new conceptual model that splits a multifunctional unit into a set of seeds with each functional group, assembling the branched elements after the independent propagation of each seed. Accordingly, the propagation steps of each element are described as dynamic balance equations in terms of the moments of the number chain length distribution. Analysis of the simulation of a batch sulfonated poly(aryl ether ketone) copolymerization process with trifunctional units is performed with the proposed model. The simulation results show that the proposed model reflects the characteristics of real copolymerization processes.

1. Introduction

The significance of branching in polymerization has been recognized over the last 40 years after, at first, being considered a side reaction. Today, controlled branching polymerization plays an important role in the design of macromolecules and functional materials [1]. The dense structure of branched polymers offers unique mechanical and rheological properties [2–4], which have potential applications in catalysis [5,6], drug and gene delivery [7,8], proton exchange membranes [9,10], and nanotechnology [11,12].

Theoretical interests in the configuration (e.g., molecular size and weight distribution) of branched polymers date back to the 1940s. During this period, Flory et al. developed statistical mechanics to calculate the molecular size distribution of three-dimensional polymers with multifunctional branching units and introduced the concepts of the degree of branching and highly branched species [13–15]. In 1952, Flory additionally developed a statistical model for highly branched polymers synthesized from AB*m*-type monomers containing an A functional group and *m* B functional groups that can react with A [16]. These statistical methods have been used in many polymerization studies involving branching units [17–20]. In addition, several other methods have been developed to obtain the configurations of branched polymers, and a set of differential equations can be used to represent the kinetic expressions [21–23]. The mean-field approach approximates the influence of individual elements on the other elements as a constant field in time, wherein each particle is independently affected by this mean-field. Thereby, this approach reduces many interactions to a single interaction [24–27]. The lattice method performs Monte Carlo simulations of 2D or 3D lattice models, wherein each square or cubic lattice is occupied by a monomer or a segment of a polymer that is then allowed to react with its neighbors [28–30].

Recent studies have mainly focused on the configuration of highly branched polymers with dendritic architectures such as dendrimers and hyperbranched and hypergrafted polymers from AB*m* or ABC-type monomers, while branched polymers with

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http://dx.doi.org/10.1016/j.polymer.2017.08.011
0032-3861/

branched architectures from linear and branched elements are still in development. There have been many studies on branched sulfonated copolymers, which have higher proton conductivities and lower methanol permeabilities than those of linear sulfonated copolymers; furthermore, these polymers have excellent properties for use as proton exchange membranes (PEMs). Zhang et al. synthesized branched sulfonated poly(aryl ether ketone) copolymers based on 6F-BPA, DFBP, SDFBP, and TFBP [31]. Wang et al. prepared partially fluorinated branched sulfonated poly(ether ether ketone)s by introducing 1,3,5-tris(4-fluorobenzoyl)benzene as the branching agent [32]. Wang et al. synthesized a series of branched sulfonated poly(ether ether ketone)s containing propenyl groups using a nucleophilic polycondensation reaction [33]. However, because the branched polymers in these studies are formed by copolymerization with multifunctional units and various types of linear monomers, existing methods cannot derive the configuration of the branched polymers because they consider the statistical properties of the growth of only one element or polymerization from one component.

This study proposes a modeling strategy that can systematically calculate the configurations of branched polymers formed by the copolymerization of various types of linear monomers with multifunctional units. The proposed method is based on a conceptual model that splits a multifunctional unit into a set of seeds with each functional group. Each seed goes through independent propagation steps that are then reassembled to yield a branched element. The propagation steps of each element are described by dynamic balance equations in terms of number chain length distribution (NCLD) moments.

This paper is organized as follows. Section 2 proposes the conceptual model for polymerization with multifunctional units, presents the propagation of seeds, and describes the assembly process wherein propagated stems and connectors are assembled into branched elements. The simulation results and their analysis in terms of each step of the model are also presented. In Section 2.1, detailed reaction kinetics, the classification of propagated elements, and the moment rate equations for linear chains, stems, and connectors are derived. Then, the molecular weight distributions (MWDs) for each element are computed numerically using the moment rate equations. In Section 2.2, the assembly state is defined, and the propagation probabilities from the initial state to each assembly state are derived using a binomial probability distribution as a function of the mole fractions of stems, seeds, and connectors. Then, the mole fractions of each branched element, classified by the number of multifunctional unit components, are calculated from the assembly state distribution. The overall MWD of the elements is obtained from the MWDs and the mole fractions of linear chains and branched elements. Finally, Section 3 provides concluding remarks.

2. Model construction and simulation analysis

Fig. 1 shows the proposed conceptual model for the polymerization process with multifunctional units. This conceptual model is based on the recognition that a branched element is a collection of linear units of similar shape, and the linear units have a multifunctional unit at their boundaries. The conceptual model first splits the multifunctional units into seeds that have one functional group. For example, the trifunctional unit in Fig. 1 forms three seeds. In the propagation process, the seeds independently propagate into stems or connectors. The stems have one seed and one functional group at both ends, whereas the connectors are those with two seeds. In conventional moment methods of the polymerization processes, elements are generally classified according to the types of the reactive functional groups of each element [34–37]. In the absence of multifunctional units, the numbers of reactive functional groups and the classification of the elements remain constant, but in the presence of multifunctional units, those of the branched elements increase infinitesimally as branching proceeds. For this reason, it has been considered that the conventional moment methods are not suitable for describing the branched polymerization systems. However, the numbers of functional groups in the stems and connectors do not change during the propagation step. This allows for the use of the conventional moment method. In the assembly step, branched elements are assembled through the combination of stems and connectors.

To illustrate the modeling framework, a batch sulfonated poly(aryl ether ketone) (SPAEK) copolymerization process with three

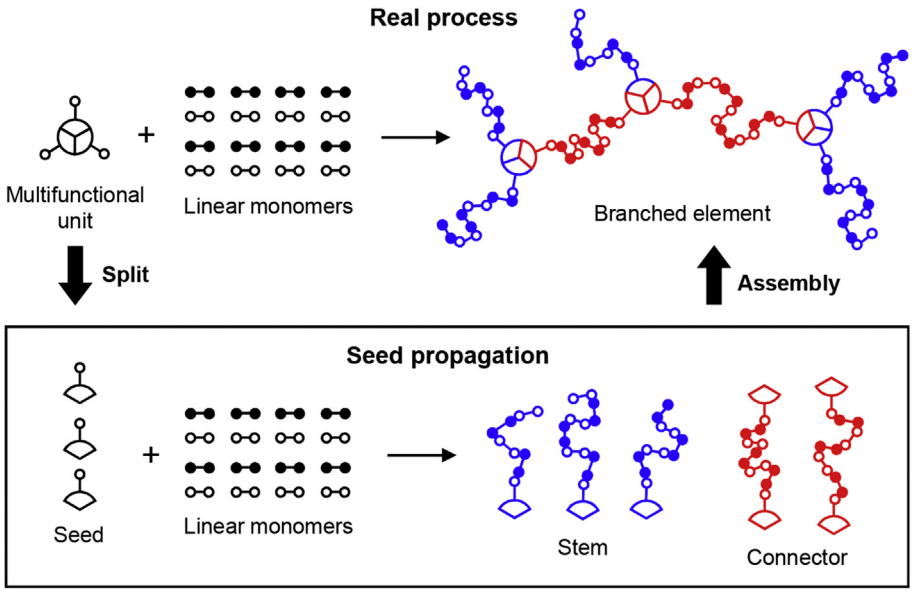

Fig. 1. A conceptual model for the polymerization of linear monomers in the presence of multifunctional units. The model decomposes multifunctional units into the seeds that propagate independently to form stems and connectors. The stems and connectors are re-assembled to represent branched elements.