A New Look at Kinetic Modeling of Nonlinear Free Radical Polymerizations with Terminal Branching and Chain Transfer to Polymer

Rolando C. S. Dias[†] and Mário Rui P. F. N. Costa*[‡]

LSRE, Instituto Politécnico de Bragança, Quinta de S. Apolónia, 5300 Bragança, Portugal,
LSRE, Departamento de Engenharia Química, Faculdade de Engenharia, Universidade do Porto,
R. Roberto Frias, 4200-465 Porto Codex, Portugal

Received July 18, 2003; Revised Manuscript Received September 5, 2003

ABSTRACT: The authors' previously developed method for the general kinetic analysis of nonlinear irreversible polymerizations based on moment generating functions is used for simulating free radical polymerization systems in which terminal branching and chain transfer to polymer are present, leading possibly to gel formation. The numerical solution of the equations needed for postgel predictions of sol fraction and average molecular weights (a major difficulty) is discussed with some detail. Finally, some different combinations of kinetic parameters were tested in order to assess their influence on the molecular weight development in a batch reactor.

Introduction

It is well-known that in free radical polymerizations long chain branching can occur due to propagation on terminal double bonds and transfer to polymer. Vinyl acetate polymerization is one of the most representative systems in which transfer to monomer creates a terminal double bond and a radical located in the methyl substituent group. Subsequent addition on the terminal double bond leads to branched polymer molecules. In addition, this system is also characterized by transfer to polymer via the reaction of chain radicals with active centers in the polymer, namely, a tertiary hydrogen on the substituted chain carbon or a methylenic hydrogen in the methyl acetate group. As a result, trifunctional units are formed in the structure of the polymer.[1,2]

In other systems, such as ethylene, methyl acrylate, vinylidene fluoride, and vinylidene chloride polymerizations, branching also occurs involving other or a subset of the mechanisms related with terminal double bond branching and transfer to polymer.[3] In some cases, termination by disproportionation is also an indirect source of branching. If the terminal double bonds generated by this mechanism have some tendency to propagate, then additional branching occurs in the polymer.

Free-radical polymerization is kinetically controlled. As the condition for random branch points in a statistical gelation process cannot be applied, with errors becoming important as soon as substitution effects are present,[4] this fact invalidates the mathematical treatment of these systems by the theory of branching processes.

Following Bamford and Tompa's pioneering work,[5] some derivations for kinetic models taking into account terminal double bond polymerization and transfer to polymer have been done,[6,7] in particular for the vinyl acetate polymerization.

These models were derived using some mathematical approximations which became widespread:

(A) Quasi-steady state for radical concentrations.

(B) Negligible presence of multiple radical centers.

(C) Negligible initiation and termination reactions relative to the propagation and transfer mechanisms.

Additionally, a closure condition is needed for solving the equations for the moments. In more recent works, the need for approximation C was avoided, but the other two simplifications are used.[8,9]

Many key features of kinetic modeling of nonlinear free radical polymerizations have been acknowledged by Kuchanov and Pis'men,[10] namely the need of avoiding quasi-steady-state hypothesis for radical concentrations and the usefulness of consideration of multiple radical centers. Nevertheless, in current methods used to describe this kind of systems some of these approximations have been kept: published works using the method of moments,[11] the numerical fractionation technique,[12] and Galerkin finite-elements method[13] have made use of approximations A and B above.

Monte Carlo simulation has the advantage of providing a detailed view of molecular structure and is a possible alternative way for dealing with these problems. Successful use with polycondensations has been known since long ago,[4] but widely different time scales in free radical polymerization make its straightforward application very time-consuming, and so it has never been carried out. Approximate Monte Carlo simulation of these same systems (and many others) has been extensively used by H. Tobita and collaborators.[14−16] It also relies on quasi-steady-state approximation and Flory's theory of branching.

The authors have been developing a more rigorous kinetic approach for modeling irreversible nonlinear polymerizations,[17] with full success for nonlinear polycondensations and nonradical polyadditions.[20] The method thus presented can be used for the prediction of average molecular weights and molecular weight distributions before and after gelation. In addition, it has been shown that elastic properties of the gel can also be calculated. Meanwhile, this approach was ex-

---

* To whom all correspondence should be addressed.

[†] Instituto Politécnico de Bragança. Fax: 351273313051. E-mail: rdias@ipb.pt.

[‡] Universidade do Porto. Fax: 351225081666. E-mail: mrcosta@fe.up.pt.

10.1021/ma035030b CCC: $25.00