



**2006 AIChE
ANNUAL MEETING**



November 12-17, 2006
San Francisco, California
San Francisco Hilton



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520b Dynamic Prediction of Microstructure and Molecular Size in Coordination Terpolymerizations Including Cross-Linking and Branching

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The production of terpolymers using coordination catalysts is a subject with a great industrial importance, being the ethylene-propylene-diene (EPDM) the most representative chemical system within this class of polymers^[1-4]. For technical reasons, only a very low content (less than 2 mol %) of diene monomer (such as ethylidene norbornene (ENB)) can usually be incorporated in the terpolymer. Chain branching and cross-linking, leading eventually to gel formation are important limiting factors to increase the diene content as desired to obtain products with improved properties.

The choice of the cyclic structure of the co-monomer is an important issue for the control of the properties of the obtained materials. For this reason, nowadays a significant research effort in this area is devoted to co- and ter- coordination polymerizations involving different cycloolefins and cycloolefins^[5] (such as 2,5-norbornadiene (NBD) and dicyclopentadiene (DCPD)). Due to branching and cross-linking reactions, gelation was also experimentally observed in this kind of chemical systems. Besides, the production of new functionalized polymers is another important area for the application of this class of polymerizations. The incorporation of an aromatic monomer like styrene is expected to be of great interest to produce versatile materials for many industrial applications. In this context, the terpolymerization of ethylene with dicyclopentadiene and styrene has been recently reported^[6].

For non-linear irreversible polymerizations, the solution of the population balances of polymer species obtained from the involved kinetic schemes can be obtained in an automated way starting with the method of the characteristics^[7-8]. This general kinetic method can deal with complex polymerization schemes even after gelation and is free from several simplifying assumptions used in the description of this class of polymerization systems: moment closures, absence of multiple active centers (such as poly-radicals), quasi-steady state for the concentrations of active centers, chain transfer only to "dead" polymer, cross-linking only of "dead" chains, the long-chain hypothesis, and so on. Comparisons of the predictions of the present approach with alternative techniques (pseudo-kinetic method, Monte Carlo, the classical method of the moments and numerical fractionation) has shown that the use of these approximation conditions can have important deleterious effects and therefore an improved accuracy and reliability in the calculations can now be obtained^[8-11].

In the present work this kinetic method is applied to the analysis of general coordination terpolymerizations including cross-linking and branching in their kinetic schemes. Generic chemical systems are considered (no particular one is selected) and the often found situation where two monomers with a single double bond (such as ethylene and styrene) and a diene (such as dicyclopentadiene) are polymerized is considered. Five different active centers in the polymer are supposed to exist and two kinds of double bonds (pendant and terminal) are considered. The kinetic scheme comprises the following generic steps: catalyst activation, initiations of the monomers and polymer double bonds, propagations (5 active centers \times 5 kinds of double bonds), β -hydride eliminations (with terminal double bonds formation), transfers to agent and co-catalyst, poisoning and deactivation and transfers to monomers (also with terminal double bonds formation). In this situation, a total number of 72 chemical reactions are considered. The automation of the simulation method allows analyzing some particular chemical system as a special case of this general case study.

It is shown that even in these complex conditions it is possible to carry out the prediction of chain length distributions (CLD, mono or multidimensional) before and after gelation (if it occurs). Recent developments concerning the prediction of sequence length distributions (SLD) and mean-square radius of gyration (RG) for non-linear irreversible polymerizations are also applied to this case study. This allows a dynamic prediction of the micro-structure and molecular size of this kind of polymers which can be useful in practice in order to have a deeper insight on the properties of the networks formed and to improve the estimation of kinetic parameters of these polymerization systems.

References

- [1] Cozewith, C., "Transient response of continuous-flow stirred-tank polymerization reactors," *A.I.Ch.E. J.*, **34**, 272 (1988).
- [2] Dolatkhani, M., H. Cramail, and A. Deffieux, "Linear non-conjugated dienes from biomass as monomers in EPDM synthesis, 2: Comparison with 5-ethylidene-2-norbornene monomer," *Macromolecular Chemistry and Physics*, **197**, 289 (1996).
- [3] Haag, M. C., J. H. Z. Santos, J. Dupont and A. R. Secchi, "Dynamic simulation and experimental evaluation of EPDM synthesis with Et(Ind)₂ZrCl₂/MAO Catalyst System," *J. Appl. Polym. Sci.*, **76**, 425 (2000).
- [4] Li R., A. B. Corripio, K. M. Dooley, M. A. Henson and M. J. Kurtz, "Dynamic modeling of crosslinking and gelation in continuous ethylene-propylene-diene polymerization reactors using the pseudo-kinetic constant approach," *Chem. Eng. Sci.*, **59**, 2297 (2004).
- [5] Naga N., "Copolymerization of ethylene with cycloolefins and cycloolefins by a constrained-geometry catalyst," *J. Polym. Sci.*, **43**, 1285 (2005).
- [6] Li, X. and Z. Hou, "Scandium-catalyzed copolymerization of ethylene with dicyclopentadiene and terpolymerization of ethylene, dicyclopentadiene, and styrene," *Macromolecules*, **38**, 6767 (2005).
- [7] Costa, M. R. P. F. N. and R. C. S. Dias, "A General Kinetic Analysis of Non-Linear Irreversible Copolymerizations," *Chem. Eng. Sci.*, **49**, 491 (1994).
- [8] Costa, M. R. P. F. N. and R. C. S. Dias, "An Improved General Kinetic Analysis of Non-Linear Irreversible Polymerizations," *Chem. Eng. Sci.*, **60**, 423 (2005).
- [9] Dias, R. C. S. and M. R. P. F. N. Costa, "Transient Behavior and Gelation of Free Radical Polymerizations in Continuous Stirred Tank Reactors" *Macromol. Theory Simul.*, **14**, 243 (2005).
- [10] Dias, R. C. S. and M. R. P. F. N. Costa, "A New Look at Kinetic Modeling of Nonlinear Free Radical Polymerizations with Terminal Branching and Chain Transfer to Polymer," *Macromolecules*, **36**, 8853 (2003).
- [11] Costa, M. R. P. F. N. and R. C. S. Dias, "Prediction of Sol Fraction and Average Molecular Weights after Gelation for Non-Linear Free Radical Polymerizations Using a Kinetic Approach," *Macromol. Theory Simul.*, **12**, 560 (2003).