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Concentration and Chain Length Effects on Block Formation during Chain Shuttling Polymerization for Product Quality Enhancement Investigation

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Abstract— In this study, numerical experimental results of block formation in chain shuttling polymerization are utilized to find and investigate the behavior and effect of trend of length variations of chain length with variation in concentration on number of blocks when polymerization. Subsequent to many validation steps, finalized rules were constructed and implemented. Results found are plausible with data and suitable to further investigate and explore the polymerization system in more detail to find out its features related to block structure.

Index Terms—Block Formation, Chain Length, Fuzzy Logic, Polymerization

I. INTRODUCTION

Polyolefins, the most growing industrial polymers, are of great interest to polymer society and the liveliest areas in polymer research to date because of their chemical structures' simplicity and fascinating hierarchical structural organizations possible. Such relatively simple polymers are used in as diverse applications as human bone prosthetic implants, gas pipelines, car bumpers, synthetic fibers, and plastic films, just to mention a few.[1]-[3]. Worldwide production of polyolefins is over 100 million ton per year. Global sales volume for 2006 was about 60 billion pounds of HDPE and 40 billion pounds each of LDPE and LLDPE. Polyolefins like other plastics are produced from oil components and could be discussed as an intermediate use of crude oil as solid hydrocarbons. These materials exhibit excellent physical and mechanical properties. However, their weak adhesion and their incompatibility with other materials limit their applications in fields where more expensive polymers are currently used. The modification of polyolefins and their development has been both an academic and an industrial challenge during last few decades [4], [5].

An extensive study of mathematical modeling in olefin polymerization reactors and polyolefin microstructure is done in [6], [7] and [8]. Also simulation of reactor cascades [9], including effects of residence time distribution on particle size distribution [10], development of analytical solutions for the trivariate distribution of molecular weight, chemical composition, and long chain branching of polyolefins made with single [11], [12] and dual [13] single-site catalysts via terminal branching were studied by the Soares group. Numerical solutions for the long chain branching (LCB) structure of polymers made with dual metallocene catalysts in the presence of LCB formation are studied in [14] and [15]. Few advances in living olefin polymerization catalysis are block copolymer formations made by fluorinated bis(phenoxy-imine)Ti complexes (fluorinated Ti-FI catalysts) [16] and use of chain-shuttling polymerization strategy to reduce the problems associated with preparation of poly-olefin block copolymers. In this strategy, the growing polymer chain is passed between catalyst sites, such that portions of a single polymer molecule are synthesized by at least two different catalysts. This strategy can be used to prepare block copolymer from a common monomer environment by using a mixture of catalysts of different selectivity's, namely monomer selectivity or stereo selectivity [17]. Chain-shuttling technology enables to produce block copolymers consist of crystallizable ethyleneoctene blocks with very low comonomer content and high melting temperature, alternating with amorphous ethyleneoctene blocks with high comonomer content and low glass transition temperature [18]. In this process, portions of a single polymer molecule are synthesized by two catalysts. Different microstructure segment contained block copolymers can be prepared (e.g. semi crystalline, hard/



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amorphous, soft) by transferring polymer chains from one catalyst to the other. A chain shuttling agent facilitates to combine different mechanical properties in one polymer chain. Precise control over polymer microstructure is the fundamental advantage of this approach [19]. Chain transfer agents are often used to terminate a growing polymer chain while creating a new site for propagation. Chain shuttling implies that the agent swaps growing polymer chains between two active catalysts producing a linear multiblock copolymer that contains alternating hard and soft block.

II. PROCEDURES AND MODELS

Chain shuttling polymerization has many reactions with complex mechanism. This mechanism and reactions are modeled using a stochastic dynamic method. Results of different parameters with respect to concentration and time followed good trend. Reaction rate constants and chain shuttling rate constant gave plausible results. Polydispersity index and molecular weight distributions are well compared with theory. In this polymerization, block formation of hard and soft monomers has been observed experimentally. The data obtained with our model for block formation during chain shuttling is scattered and unresolved by the model in first instance. Deep programming may be needed to present out this portion of the model. Another solution is that to use some other technique for this portion of the problem. Unswervingly fuzzy logic is approached and data obtained from previous built model is fed to fuzzy tool to train and test and then to obtain the solution. Solving polymerization process problems a lot of work has been done using different stochastic based techniques. Reference [20] discussed different criteria for successful applications of fuzzy control to numerous industrial applications reviewing the previous work in the field. Reference [21] studied the application of fuzzy logic in the control of polymerization reactors. Reference [22] applied artificial neural network models to control a time variant chemical plant. Reference [23] studied the trajectory tracking in batch processes using neural controllers. Reference [24] reviewed application of artificial neural networks to polymer composites. Reference [25] studied the adaptive heuristic temperature control of a batch polymerization reactor. Reference [26] investigated an industrial case study incorporating prior knowledge into artificial neural networks. Reference [27] studied data-driven model based control of a multi-product for semi-batch polymerization reactor. Reference [28] evaluated neural networks-based controllers in batch, polymerization of methyl methacrylate. Reference [29] studied ANN-based soft-sensor for real-time process monitoring and control of an industrial polymerization process. In this work Chain shuttling polymerization has been studied. It has many reactions with complex mechanism. This mechanism and reactions are modeled using a stochastic dynamic method, Monte Carlo method. The block formation in the said polymerization is studied for different monomer concentrations as shown in Figure 1.

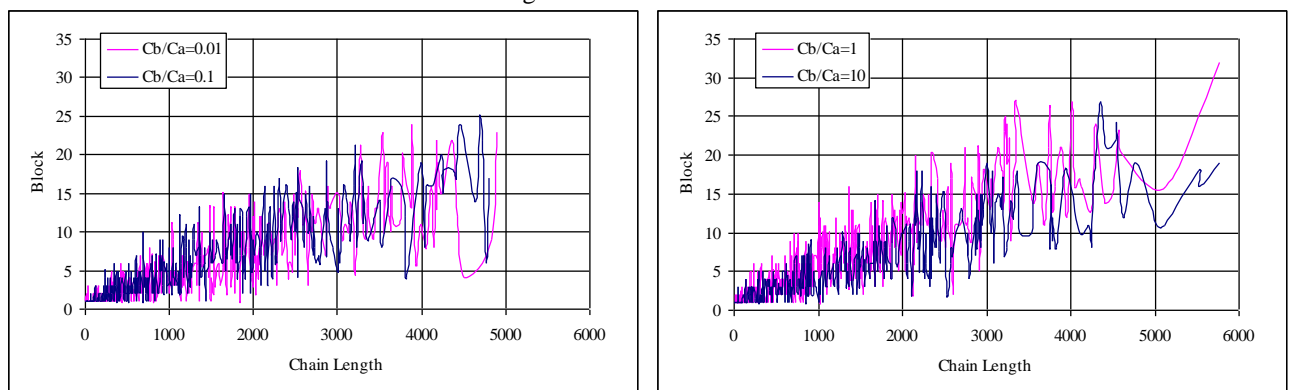


Fig 1: Plots of numerical experimental results of block formation, for $C_b/C_a = [0.01, 0.1, 1.0, 10]$ with $C_a=0.1$ and $C_b = [0.001, 0.01, 0.1, 1.0]$

This modeling work is based on numerical experiments done using a stochastic Gillespie's algorithm [30] for dynamic Monte Carlo simulation. The term was coined by S. Ulam and N. Metropolis in reference to games of chance, a popular attraction in Monte Carlo, Monaco [31], [32]. It is a method for iteratively evaluating a deterministic model using sets of random numbers as inputs. Such simulations increase both scientific understanding as well as served as an informatics tool to evaluate and design new processes and methods. The dynamic model was used to predict monomer conversion, average molecular weight, polydispersity index, and copolymer composition as a function of polymerization time. The model can also predict the distribution of molecular weight, chemical composition, and comonomer sequence length at any polymerization time or

comonomer conversion. The simulation was used to explore the effects of rate constant values and reactant stoichiometry on the microstructure of chains elsewhere. Extensive runs were simulated and data was collected. Figure 1 shows the selected results of which a portion of data is so clustered that fuzzy logic is approached to deal that portion. The results may be used for any polymerization system using chain shuttling agent for block formation. A reasonable calculations and material selection to modify the chain structure and polymer morphology may be made in view of these results. Other chemical reaction mechanism may also be fuzzify in the same manner to control and explore the process conditions.

Matlab is a power full tool which is used to run fuzzy logic programming. Type of fuzzy input system was chosen as Mamdani. Defuzzification was done by *centroid* method. Membership functions were selected *trimf* for each FIS. Rules were made and supported by data produced from research experiments for block formation of different chain length for varying monomer concentration with constant catalyst concentration. Table 1 shows the ranges used for data inputs and output.

Table 1. Type and range of Different Variables

Variable	Type	Minimum	Maximum
Concentration, mg/L	Input	0	100
Chain length	Input	0	6000
Number of blocks	Output	0	20

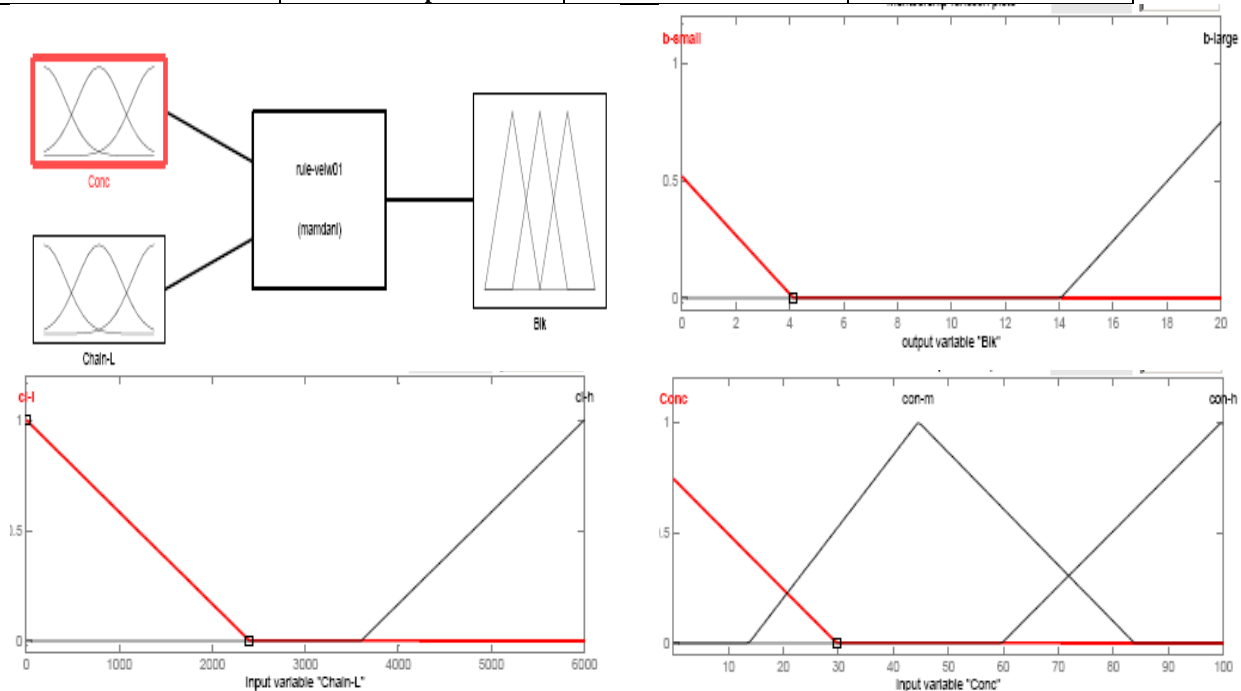


Fig 2: Diagram of FIS System Input Output Variable Range Setup for Constructing and Verifying Rules

III. RESULTS AND DISCUSSION

Mamdani type Fuzzy Inference System is selected and concentration, chain length, are set as input variables whereas number of block formation as out put variable. Membership functions of type time are defined for all inputs using centriod defuzzification. Ranges are defined for all variables as shown in Table 1. Rules are defined on the basis of data extracted from preliminary numerical experiments. Those rules are implemented with full weight given to each rule. Figure 2 shows the diagram of system followed. Two input variables are fed to mamdani FIS and output is received at the other end. Any variable can be changed, modified and its range can be set to a different number at any time to study the effects of range change on out put. This range change step is a validation step to check the rules fed to system. It is found that range change resulted in good agreement with set rules. It is also noted that causal importance is highly involved in this system. Rules are implemented and their membership functions plots are also shown in Figure 2. Range of concentration is set into lower, medium and upper where as chain length range is set into lower and higher correspondingly. These divisions of input variables then use to create rules

combining with output variable lower and higher range distribution. Numerous possibilities played on these plots to satisfy the data and theory and to find acceptable link between them.

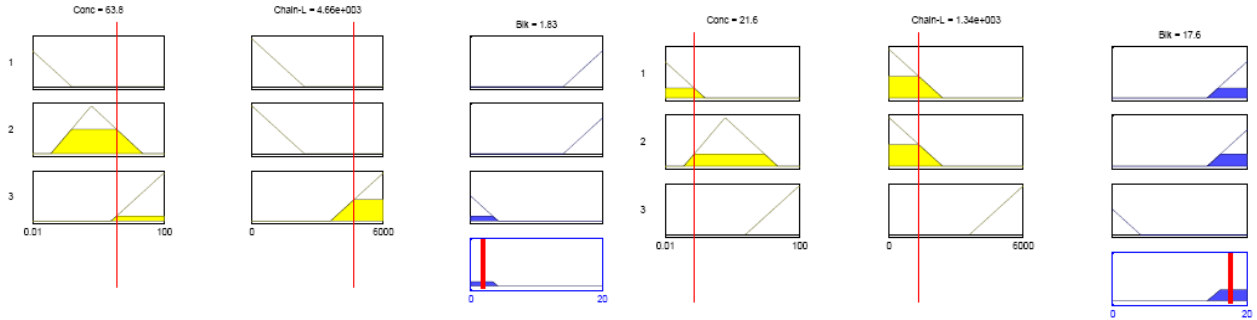


Fig 3: Display of Rules on Fuzzy Mamdani FIS System

These fuzzy performances also show that the rules set are acceptable and there's no mess up to go for results. The rules made are displayed in Figure 3. It is also observed that after numerous performances of validation checks of data and rules the system formed is better to understand the problem. Figure 4 show the surface plot results which explain all the trends implemented from data to fuzzy system.

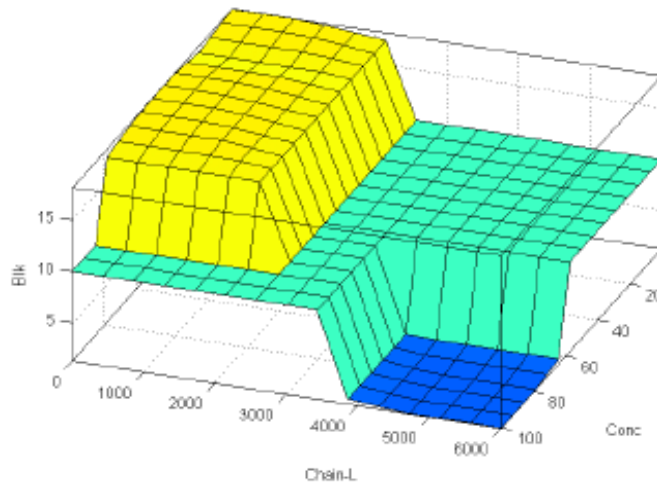


Fig 4: Surface out Put Graph of Block Formation at Different Concentration for Various Chain Lengths

These results are plausible with the preliminary numerical experimental results and promising to study for new data system or polymerization system. At higher concentration and at higher chain length, number of block is lower. At higher concentration and at lower chain length, blocks are more. Similarly at higher concentration blocks are higher as well as chain length is higher. Range analysis of the surface plots agreeing the preliminary numerical experimental results. Imagining the work at scale up from microstructure to mega structure, building the enormous materials at field out of the laboratory, replicating the very detail, it is very necessary to point in each and every step. Every structure needs a block to start as well as to complete and finalize the whole. Race to revenant material formation of long chain branches may be initiated depending upon different end user applications. A phenomenon may occur of destroying puny chains to build more exact, stronger, and more application oriented structure of enhanced quality polymer blocks to build an overall acceptable and passed as commercially stable material. In first phase, it is liked to have best quality material with full reproduction of same quality product. A rigorous production keeping the quality consistent is always welcomed. It is also depicted that the details of the block in front and the block behind a block should be implicit. Some times surface shine is required sometimes it is not. Surface par may be controlled to show weathering effects on newly constructed material to modify its texture. Glass may be looked like water or so hard to be survived in the space. Medium of reacting system can play a major part. A block may be hard in one neighborhood of the medium whereas crossing the inner borders it may become soft. Even its segments may change their characteristics.



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IV. CONCLUSION AND RECOMMENDATION

Block itself also has portion of soft and hard segments. These preliminary studies have explored the complex problem of block formation in the sense that now the relation between chain length and concentration with number of blocks can be used for further implementation to real and actual system without doing and repeating costly experiments in the lab. Further studies can be done to explore deep into block structure using suitable AI technique. Other methods along with fuzzy may give some more understanding of the system. Rules were assigned full weights to each one. Effect of fraction of weight of each rule may also be studied. Quality enhancements may be controlled before hand with this verge on near-perfect approach.

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