An Integrated Model-Based Analysis of Polymer Chemistry and Polymerisation Reactors

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Summary: In this paper, a simple demonstration is presented on the analysis of the combined effect of polymer chemistry and the polymerisation reactor on the polymer properties. The model would ideally account for the raw material and end-product characteristics and properties on the one hand; the polymerisation kinetics and reaction engineering on the other hand. This system-wide model-driven approach enables the interlinking of the widely disparate facets of polymer science and engineering, and thereby provides a tool for rapid and efficient identification and scale-up of new polymeric materials that would be exploited in future studies. The ideas are demonstrated with regard to a hyper-branched polymerisation chemistry.

Keywords: hyperbranched; modeling; multi-functional monomers; process sensitivity; reachability analysis

Introduction

It is well known that polymers are products-by-process.[1] In other words, the reactor and also the subsequent processing steps play a crucial role along with the chemistry in determining the structural and functional properties and with it the end-use properties. This aspect renders the approach sub-optimal to decouple synthesis and characterisation/performance function for end-use properties from the reaction engineering and scale-up activities. It becomes imperative to incorporate the reactor characteristics in the process of identification of polymerisation reacting conditions and stoichiometry for polymer synthesis.

This paper presents some preliminary studies that would form the basis for one such integrated strategy for the identification of new polymeric materials.[2] The strategy is based on a generic model that incorporates the polymerisation kinetics and generic reactor characteristics with the raw material and end-product properties. The use of the integrated system-wide model to understand the dynamic behaviour, potentials and limitations of the polymerisation kinetics is presented in this article. Such findings of the potentials, limitations and dynamic behaviour will aid the synthesis and material selection decisions through optimally-designed experimentation, as will be presented in future contributions.

The chemistry under study is a hyperbranched polymerisation. Hyperbranched polymers assume importance in view of their lower solution and melt viscosities, increased solubility and higher functional group density, thereby providing an economically-viable alternative to dendrimers within a certain performance envelop.[2] Being a relatively new class of polymers, they present several avenues for research and development in the aspects of synthesis,[3–8] characterisation,[9] and model development.[10,11] In the present study, the synthesis of a hyperbranched polymer is performed through the use of multi-functional monomers (MFM) as branching agents.[2] This route based on free radical polymerisation enables the attainment of high conversions in a one-pot synthesis

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framework and thereby renders the process economically viable.[2,6] Hyperbranched poly(-methyl methacrylate) is chosen as the test case, and is synthesised using tripropylene glycol diacrylate as the MFM. Batch free radical solution polymerisation in xylene solvent with AIBN initiator and 1-decanethiol as the chain transfer agent (CTA) have been carried out under isothermal conditions at 70 °C. The melt viscosity of the hyperbranched PMMA produced is found to be considerably different from that of a linear polymer under similar reactor conditions. See Gretton-Watson et al.[2] for further details.

Model-based Process Analysis

A dynamic mathematical model has been proposed for the hyperbranched polymerisation process and has been validated in previous studies.[2] In this section, some preliminary results on the use of the above model is presented. The aim is the identification of the chemistry that, in combination with the reactor configuration, will lead to the desired polymer properties and the best possible operating configurations. The metrics to decide upon the best configuration include wide reachability regions, most conducive operating conditions (such as linear process, desired bifurcation traits), and facilitated control (such as the availability of sufficiently-sensitive manipulations). Several of these points are illustrated here through simple examples.

Perturbation Studies

In order to understand the process dynamics, sample perturbation studies are presented here with respect to the effect of chain transfer agent (CTA) and the effect of termination-by-disproportionation. In Figure 1, the effect of the inclusion of CTA on the process kinetics is presented. It

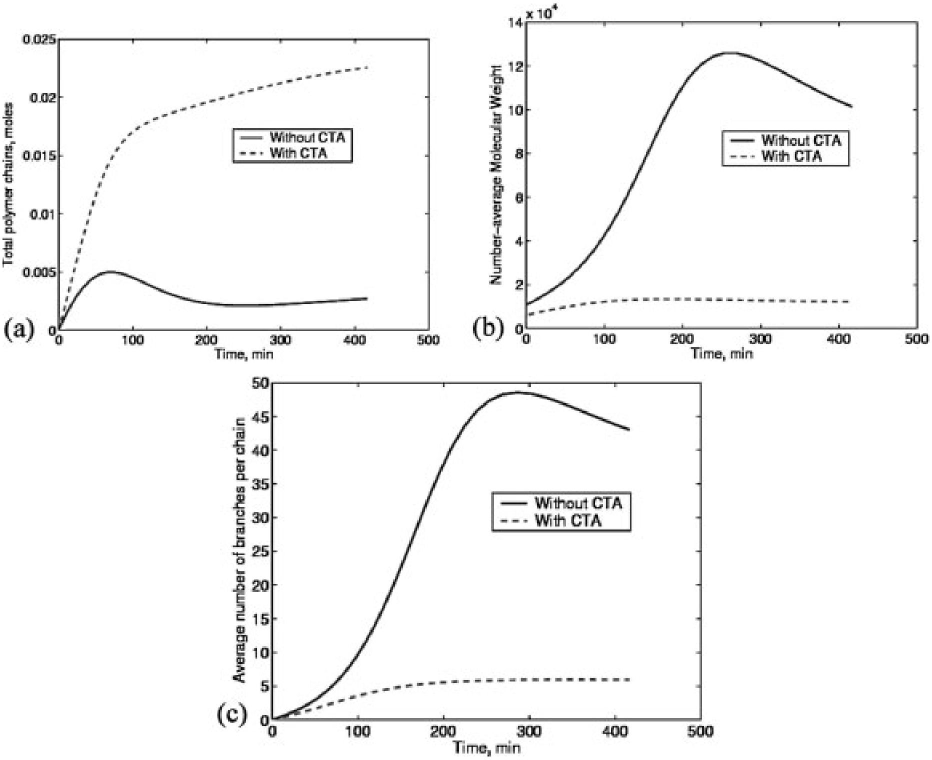

Figure 1.
The effect of the inclusion of CTA on the polymerisation and branching kinetics.

is seen in Figure 1a that there is over an 8-fold drop in the number of polymer chains – the zeroth moment of the chain length distribution, λ_0 — in the absence of CTA. This in turn leads to an increase in M_n, as seen in Figure 1b. The increase seen in M_n is balanced by the decrease in λ_0, which is expected in incorporating the chain transfer mechanism into a lumped model of average molecular weight. Information on the effect of CTA obtained from a distribution model might provide better insight into the process. It can be seen from Figure 1c that there is an increase in the average number of branches per chain in the case without CTA. This increase is however found to be smaller than the decrease in λ_0.

In Figure 2, the effect of termination-by-disproportionation is presented. When the rate constant for termination-by-disproportionation k_{td} is reduced, the relative probabilities of the other reactions that involve polymeric species are increased. Of these other reactions, the termination-by-combination and the chain transfer reactions are the ones that affect the number of chains λ_0. These two reactions affect λ_0 in opposite directions. It is seen in Figure 2a that the reduction in k_{td} leads to an increase in λ_0 at later times of the batch. This indicates that although the chain transfer and termination-by-combination reactions apparently balance each other at the early times (before 80 min), the chain transfer reaction is dominant over termination-by-combination at later times. A possible explanation is the increasing gel effect at later times of the batch. The dominance of CTA is also seen in Figure 2b, which depicts a decrease in M_n under a reduction in k_{td}. These effects are difficult to deduce by intuition and are possible to deduce only through such a system-wide

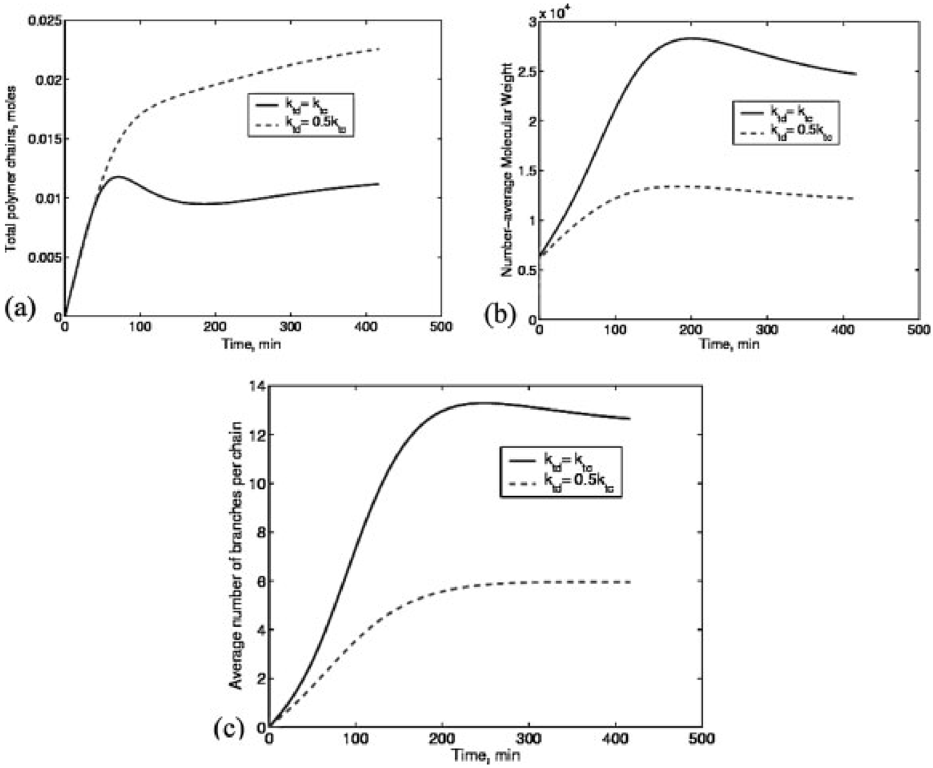

Figure 2.
The cumulative effect of termination-by-disproportionation on batch simulation results.

model. The information will be useful in the choice of CTA and other recipe, to alter the dominance to suit specific needs. The effect of the reduction of k_{td} on the average number of branches per chain is seen in Figure 2c.

Model-based Decision Making: Through Sensitivity Analysis

At the synthesis stage, it will be desirable to know the effect of the choice of the reaction mixture on the material properties. This is illustrated in a simple manner, based on the assumption that the M_n value and the degree of branching are good surrogates of the material properties in question. It is further assumed that the key kinetic constants are adequate representation of the raw material properties.

In Figures 3 and 4, the choice of the MFM is depicted by considering the effects of the self-propagation rate constant for the MFM, $k_{p\text{-}AA}$, and the effects of the chain transfer constant from the MFM-derived radical, $k_{A\text{-}cta}$. Figures 3a and 3b present, respectively, plots of the degree of branching and the fraction of unbranched MFM (MFM that have lost their potential to lead to branches). In Figures 3a and 3b, it is seen that the larger the value of $k_{p\text{-}AA}$, the larger

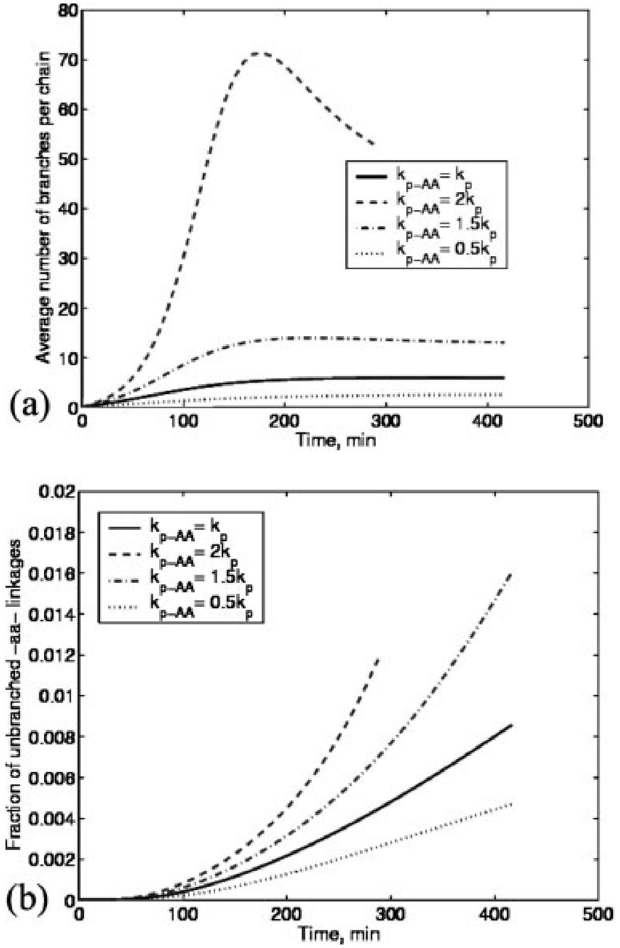

Figure 3.

The effect of the MFM self-propagation rate constant on the batch simulation results — possibility of a trade-off optimisation problem.

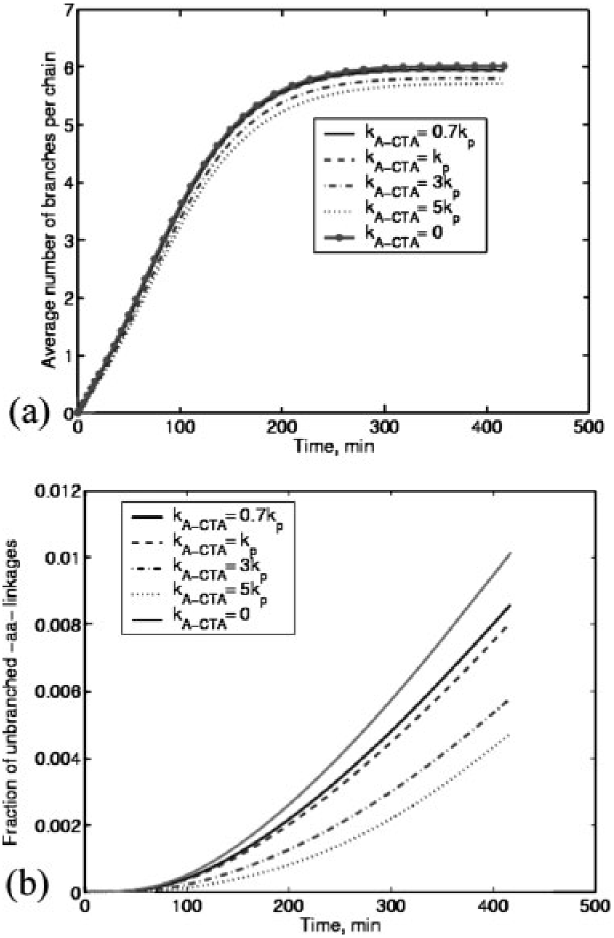

Figure 4.
The effect of the MFM chain transfer rate constant on the batch simulation results — possibility of a trade-off optimisation problem.

is the degree of branching, but the larger also is the fraction of unbranched MFM. This could indicate a clear trade-off problem in the choice of MFM. The loss fraction might need to be minimised as the MFM could be an expensive chemical specifically synthesised for this polymerisation recipe. The average number of branches per chain might need to be maximised, as a larger average of branches might indicate a larger degree of hyperbranching in this lumped model. Hence there is a clear need for a trade-off problem in the choice of the MFM. A similar trade-off is also evident in the choice of MFM with regard to the chain transfer constant and its effect on the average number of branches and the loss fraction seen in Figure 4.

Model-based Decision Making: Through Reachable Region Analysis

Model-based decision-making using the reachable regions as guides/metrics is depicted in Figures 5 and 6. The specific focus is batch operation under isothermal conditions. It is assumed that for isothermal batch operation, different choices of initial concentration of monomer and chain transfer agent are available. A simulation-based reachability analysis is performed.[12] Different combinations of the monomer and

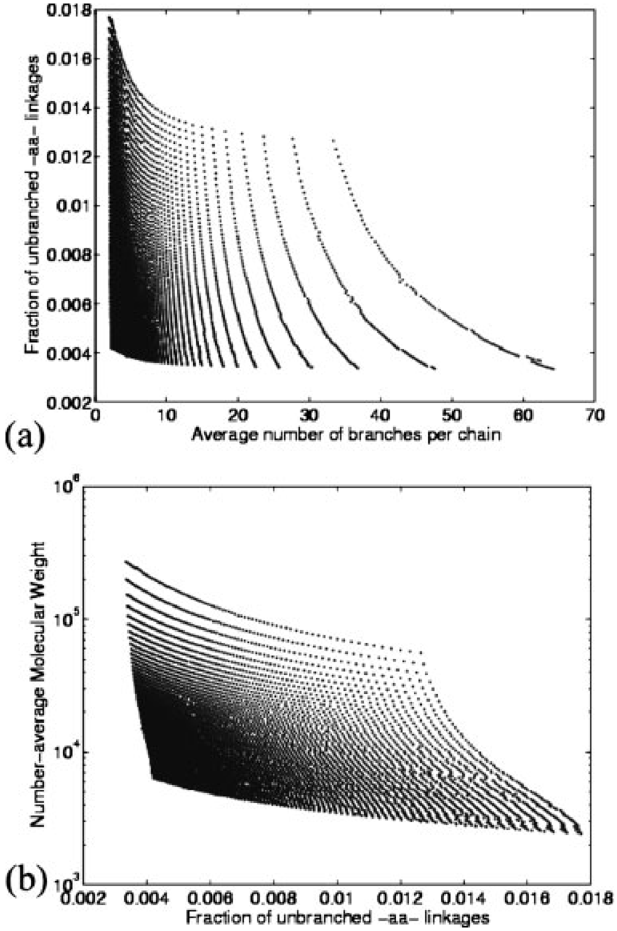

Figure 5.

Reachable regions of the property space and economy variables for a given MFM, under batch isothermal operation — the operating variables are the initial concentrations of the monomer and CTA.

CTA initial concentrations are simulated using the model and the value of the number-average molecular weight, fraction of unbranched MFM linkages, and the average number of branches per chain values from each simulation are recorded. The envelop of the reachable space is then drawn around the recorded data points, which are depicted in Figure 6. The individual reachable data points for batch operation are shown in Figure 5 for a given choice of MFM. It is observed from Figure 5b that as the target number-average molecular weight is increased, both the attainable range of fractional MFM loss as well as the values of these MFM losses are reduced. A similar observation is also made in Figure 5a with increasing average number of branches per chain. Both these effects might prove advantageous for reactor operation.

The effect of different MFMs on the reachable regions of the property spaces was examined next. Assuming that the different MFMs are distinguished by their self-propagation rate constant $k_{p\text{-}AA}$ alone, such reachable spaces are generated for two choices of $k_{p\text{-}AA}$ values. The envelop of the reachable space for the two choices of $k_{p\text{-}AA}$ values are presented in Figure 6. Note that the reachable data points presented in Figure 5 correspond to $k_{p\text{-}AA} = k_p$.

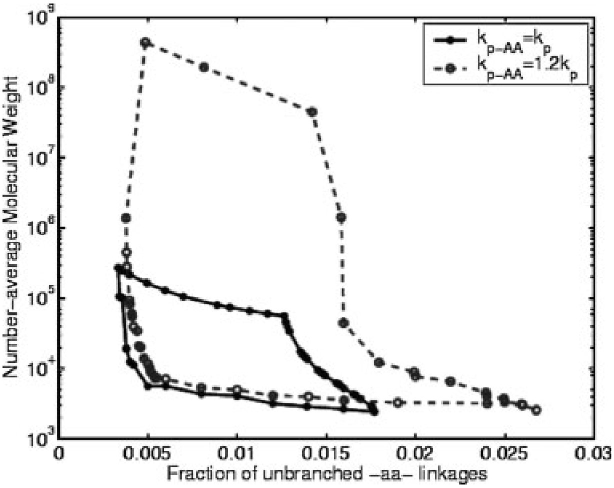

Figure 6.
The envelop of the reachable space with respect to the number-average molecular weight and the fraction of lost MFM, for different choice of MFM.

It is seen that the MFM with a larger value of $k_{p\text{-}AA}$ leads to a wider attainability. Thus, one could choose the MFM with the largest value of $k_{p\text{-}AA}$ that is economically available for synthesis.

It has to be mentioned that in this preliminary study, different MFMs are distinguised based on single kinetic parameters such as $k_{p\text{-}AA}$ and $k_{A\text{-}CTA}$. In a realistic framework, several of the kinetic parameters associated with the MFM will be different when switching from one MFM to another. The cumulative effect of the differences in the kinetic parameters both on the net process sensitivity and on the reachable spaces could be considerably different. Such more rigorous analysis will be pursued in future.[13]

Conclusions

This article presents some preliminary demonstration on the use of an integrated system-wide model for dynamic analysis, which could provide useful information for the synthesis of new polymeric materials. The basic tenet is that the properties of polymeric materials are determined by both the polymerisation recipe and the reactor. Thus, an integrated model that accounts for the raw material properties, end-use properties and the reactor characteristics provides an ideal mechanism to simultaneously identify the optimal ingredients that will lead to polymers with desired properties and also ensure good operability and controllability of the process. In particular, the use of the system-wide model to identify the polymerisation recipe was discussed. The two simple metrics (decision factors) considered here are the process trade-off (material property *versus* economy) and reachability region analysis (breadth/range of end-product properties). The former highlighted the possibility of pareto-optimisation to identify a trade-off recipe. The latter was demonstrated for a batch isothermal reactor. Future studies will include more exhaustive reactor configurations and raw material properties. It will also include the consideration of the process dynamics, sensitivity and controllability (ease of control) into the decision-making process.

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