

Introduction

- The objective of this presentation is to compare several dynamic modeling techniques to describe the polymerization of monomers, such as styrene, with mono- and bifunctional initiators and the time evolution of their chain length distributions.
- Three methods are used for comparison:
 - ✓ Method of moments.
 - ✓ Instantaneous properties method (only for monofunctional initiator).
 - ✓ Dynamic Monte Carlo simulation.

Table 1 - Kinetic parameters and physical constants for styrene, BPO, and L-331.

Styrene

$$k_{th} (\text{L}^2 \text{mol}^{-2} \text{min}^{-1}) = 1.314 \times 10^7 \exp(-27,440.5 / RT)$$

$$k_p (\text{L mol}^{-1} \text{min}^{-1}) = 6.128 \times 10^8 \exp(-7067.8 / RT)$$

$$k_{i1} = k_{i2} \approx k_p$$

$$k_{M} (\text{L mol}^{-1} \text{min}^{-1}) = 2.319 \times 10^8 \exp(-12,000 / RT)$$

$$k_{ic0} (\text{L mol}^{-1} \text{min}^{-1}) = 7.53 \times 10^{10} \exp(-1680 / RT)$$

$$A_1 = 2.57 - 5.05 \times 10^{-3} T$$

$$A_2 = 9.56 - 1.76 \times 10^{-2} T$$

$$A_3 = -3.03 + 7.85 \times 10^{-3} T$$

$$k_{ic} = k_{ic0} \exp[-2 \times (A_1 x + A_2 x^2 + A_3 x^3)]$$

BPO (Monofunctional Initiator)

$$k_d (\text{min}^{-1}) = 7.409 \times 10^{16} \exp(-31,360.7 / RT)$$

$$f = 0.58$$

L-331 (Bifunctional Initiator)

$$k_{d1} (\text{min}^{-1}) = 1.269 \times 10^{18} \exp(-35662.08 / RT)$$

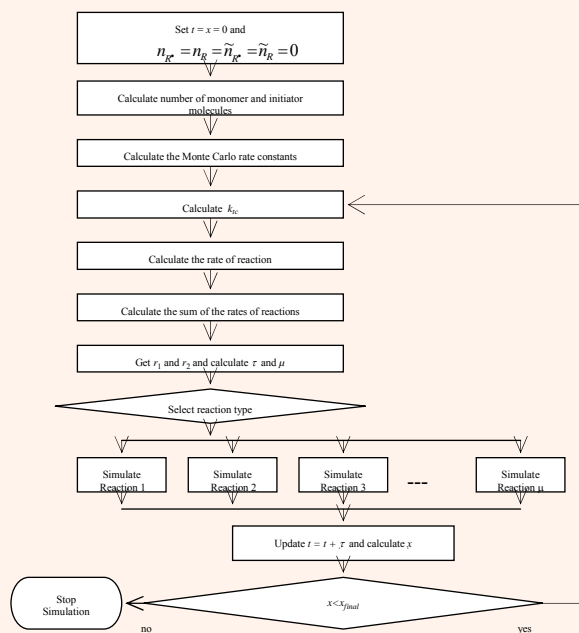
$$k_{d2} (\text{min}^{-1}) = 1.09 \times 10^{21} \exp(-42445.26 / RT)$$

$$f = 0.7$$

Conclusions

- Three methods have been investigated. All methods are in good agreement.
- The method of moments is the simplest method. It can only predict the average molecular weight properties, but not the complete CLD.
- The instantaneous properties method is much simpler to implement and much faster than Monte Carlo, but it can only be used with monofunctional initiators.
- Monte Carlo simulation is applicable for both initiators. It provides a wealth of information on polymer microstructure not obtainable from the other two techniques. Moreover, no assumptions are required, but the computational time is longer.
- All the mathematical modeling techniques shown herein are not restricted only to polystyrene, but can be easily applied to other monomers.

Figure 1 – Monte Carlo flowchart of styrene polymerization



Results and discussion:

- Figures 2 to 5 compare three techniques (Moments, Instantaneous Properties and Monte Carlo) to model styrene polymerization with monofunctional initiator (BPO) at 90°C.
- Figures 6 to 9 compare two techniques (Moments, and Monte Carlo) to model styrene polymerization with bifunctional initiator (L-331) at 100°C.
- Several process conditions have been investigated and all agree well.

Simulations

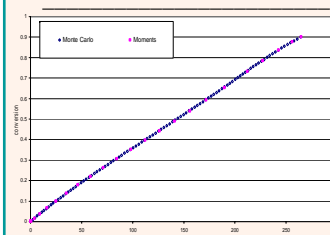


Figure 2 – Monomer conversion versus time: [BPO] = 0.01mol/L and T = 90°C

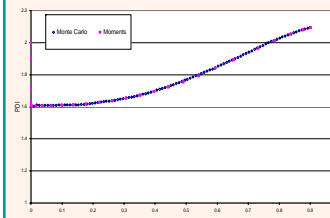


Figure 4 – Polydispersity index (PDI) versus monomer conversion: [BPO] = 0.01mol/L and T = 90°C

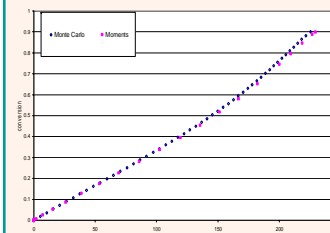


Figure 6 – Monomer conversion versus time: [L-331] = 0.01mol/L and T = 100°C

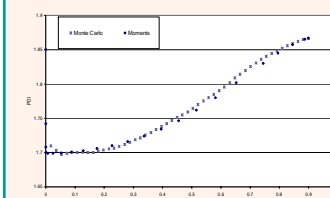


Figure 8 – Polydispersity index (PDI) versus monomer conversion: [L-331] = 0.01mol/L and T = 100°C

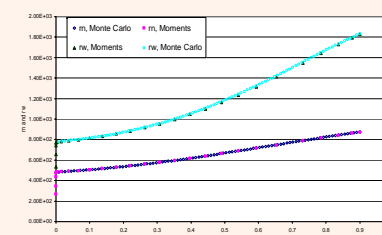


Figure 3 – Number (r_n) and weight (r_w) average chain length versus monomer conversion: [BPO] = 0.01mol/L and T = 90°C

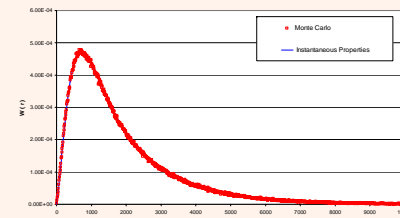


Figure 5 – Chain length distribution (CLD): [BPO] = 0.01mol/L and T = 90°C

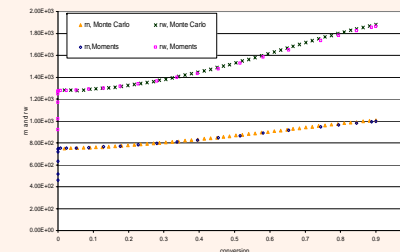


Figure 7 – Number (r_n) and weight (r_w) average chain length versus monomer conversion: [L-331] = 0.01mol/L and T = 100°C

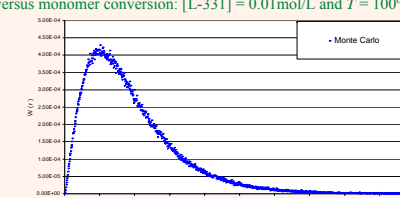


Figure 9 – Chain length distribution (CLD): [L-331] = 0.01mol/L and T = 100°C