

## Tutorial-1

April, 2023

### (Introduction to Polymer Science)

- Write down the mechanism of polymerization of styrene with the following initiators  
(a) AIBN (b)  $\text{BF}_3/\text{H}_2\text{O}$  (c) Bu-Li
- Based on kinetics, explain the effect of initiator concentration on rate of polymerization and degree of polymerization
- Why molecular weight of polymers are expressed as average molecular weights. Explain the common average molecular weights used.
- What do you understand by molecular weight distribution curve? Draw a hypothetical molecular weight distribution curve and mark the molecular weight averages on the curve.
- In a free radical polymerization reaction what would be the effect of (a) increasing  $[\text{M}]_0$  four times at constant  $[\text{I}]_0$  and (b) increasing  $[\text{I}]_0$  four times at constant  $[\text{M}]_0$  upon  
(i) Radical concentration at steady state (ii) the rate of polymerization (iii) degree of polymerization
- Free radical polymerization of ethylene under high pressure will lead to the formation of LDPE. Explain the mechanism.
- Styrene was polymerized at a mass concentration of  $300 \text{ g L}^{-1}$  in toluene using AIBN as initiator at a mass concentration of  $1.64 \times 10^{-2} \text{ g L}^{-1}$  and a reaction temperature of  $60^\circ\text{C}$ . Calculate the initial rate of polymerization and the molar mass of the styrene formed in the initial stages of the reaction if the termination happened entirely by combination. Given that the rate constants at  $60^\circ\text{C}$  are  
initiator dissociation  $k_d = 4.5 \times 10^{-6} \text{ s}^{-1}$  propagation  $k_p = 367 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  
termination  $k_t = 9.5 \times 10^6 \text{ L mol}^{-1} \text{ s}^{-1}$ , Initiator efficiency  $f = 0.7$   
Molecular weight of AIBN =  $164 \text{ g mol}^{-1}$ , styrene =  $104 \text{ g mol}^{-1}$
- A sample of polystyrene is composed of a series of fractions of different sized molecules:

Fraction	Weight Fraction	Molecular weight
A	0.10	12,000
B	0.19	21,000
C	0.24	35,000
D	0.18	49,000
E	0.11	73,000
F	0.08	102,000
G	0.06	122,000
H	0.04	146,000

Calculate the number average and weight average molecular weights of this polymer sample. Draw a molecular weight distribution curve.

- A sample of polystyrene prepared by bulk polymerization at  $60^\circ\text{C}$  using radioactive ( $^{14}\text{C}$ ) AIBN as initiator was found to have  $M_n = 1000 \text{ kg mol}^{-1}$  and a radioactivity of  $6 \times 10^3 \text{ counts s}^{-1} \text{ g}^{-1}$ . Given that the AIBN has a radioactivity of  $6 \times 10^9 \text{ counts s}^{-1} \text{ mol}^{-1}$ , determine the mode of termination which operated in the preparation of polystyrene sample.