Polymers

Example Sheet E3

Addition Polymerisation

1. Methyl methacrylate is polymerised using Benzoyl peroxide as an initiator and termination occurs by disproportionation.

   Sketch the Chemical sequence of (a) a P_1 mer, (b) a P_2 mer, (c) a M_n and M_r mer, that had terminated by disproportionation from a P_n and P_r mer.

2. Styrene is polymerised by thermal activation where the initiation rate constant is third order with respect to monomer concentration and has a value 1.6×10^{-11} $[m^3/kmol]^2$,1/s. The propagation rate constant is 567 $[m^3/kmol]$,1/s and the combination termination rate constant is given by 5.0×10^7 $[m^3/kmol]$,1/s.

   (a) Determine the kinetic chain length, $\overline{DP}_n$ and $\overline{M}_n$ for the polymerisation when [M] = 2 kmol/m^3.

   $\overline{DP}_n = 28\,350$ $\overline{M}_n = 2.96\ 10^6$

   (b) Determine values of the above parameters assuming that monomer chain transfer also occurs with a value of $k_m = 7.8$ $[m^3/kmol]$ 1/s.

   $\overline{DP}_n = 73.5$ $\overline{M}_n = 7{,}644$

3. Styrene is polymerised in the presence of an initiator Benzoyl peroxide and the initiation rate constant is second order with respect to monomer concentration and first order with respect to initiator concentration.

   Using the data given below determine the time $t_{1/2}$ in a batch reaction for the monomer concentration to drop to half its starting value for operation of the reactor at T = 120˚C and T = 140˚C. Determine the values of $\overline{M}_n$ at both temperatures for $t = 0$ and $t = t_{1/2}$

You may assume the initiator concentration remains constant at 0.1 kmol/m^3 and the initial monomer concentration is 4 kmol/m^3. Termination is by combination and chain transfer is negligible.

Data	**$k = Ae^{-E/RT}$**
Initiation	**$A = 8 \times 10^6$ $[m^3/kmol]^2$,1/s**
	E = 110 kJ/mol
Propagation	**$A = 7.2 \times 10^6$ $[m^3/kmol]$,1/s**
	E = 29.3 kJ/mol
Termination	**$A = 1.3 \times 10^9$ $[m^3/kmol]$,1/s**
	E = 10.1 kJ/mol

$\overline{M}_n$ at 120 = 568,000

$\overline{M}_n$ at 140 = 360,000

Half time at 120 = 13.3 hr
Half time at 140 = 4.0 hr

4. Tripos taster with copolymerisation 1999.3.3

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