EXERCISES TO THE LECTURE POLYMER REACTION & COLLOID ENGINEERING

SERIES 7

issue date: 21.12.2016
due date: 11.01.2017

Assistant Lecturers: Stefano Caimi*, Peter Fleckenstein†

Emulsion Polymerization

You want to carry out a seeded emulsion polymerization in a 10 L reactor. You are provided with a suspension of polymer particles with a particle diameter of $d^0_{Pol} = 50$ nm and a mass fraction of $w_{seeds} = 0.05$. You want to add $M_0 = 2$ mol/L of monomer and $w_{\mathrm{I},0} = 0.01$ of Initiator (with respect to the monomer).

a) Before you start the polymerization you have to add a certain amount of emulsifier. Calculate the minimum and maximum emulsifier concentration you can use for your experiment.

   If you add too much emulsifier in the beginning, you will form micelles and introduce undesired secondary nucleation. If you add too little emulsifier, the particles will not be sufficiently covered at full conversion and therefore destabilize. The critical minimum coverage is 0.2 ($\frac{\Gamma_E}{\Gamma^\infty_E}$). Use the mass balance $E_0 = E_w + E_p + E_M$ to calculate the minimum and maximum emulsifier concentration you can use, where E_0 is the emulsifier amount you add to your suspension, E_w is the amount dissolved in water, E_m is the amount of emulsifier incorporated into micelles and E_P is the amount adsorbed on the particle surface.

b) Before starting your experiment you want to predict the outcome. You can use equation 5.14 from the lecture notes to compute the conversion and particle size. Plot the conversion over time and particle size, volume of polymer and volume fraction of monomer in the particles over conversion.

   Since we are doing a seeded emulsion polymerization we do not need to consider the nucleation. You can assume that you are in a 0-1 system for the radicals and therefore assume the average number of radicals per particle $\overline{n} = 0.5$. The volume fraction of monomer in the particles is constant as long as there are monomer droplets. You can

*HCI F138, Tel: +41 44 633 3259, stefano.caimi@chem.ethz.ch
†HCI F130, Tel: +41 44 633 6775, peter.fleckenstein@chem.ethz.ch

find the volume fraction of Monomer in the system by solving the mass balance over the Monomer where N_{M_0} is the number of Monomer units initially in the system and N_{M_P} the number of molecules in the Particle. We can assume for all times, that the number of Monomer Units in water N_{M_W} is zero.

c) Following the polymerization you see that your computed conversion and particle size do not fit perfectly with your experiments. In the literature you find, that radical desorption from the particles actually plays a significant role in your system. Modify equation 5.37 in the lecture notes to include desorption and solve it for a pseudo steady state value of the average number of radicals $\overline{n}$. Plot $\overline{n}$ over time and replot the conversion over time and particle size, volume of polymer and volume fraction of monomer in the particles over conversion.

d) Find the instantaneous number average, $\overline{n}_{\mathrm{N}}$ and weight average $\overline{n}_{\mathrm{W}}$ for the dead chains CLD and plot the results against conversion. Compare the values for the case with and without radical desorption.

You will find the equation for the number average in the case without desorption in the lecture notes. The other case you will have to derive yourself. Just a couple of hints: You will find again that the number average molecular weight is inversely proportional to a ratio of characteristic times. In the case of a 0-1 system the termination rate does not influence the chain length. Instead it is controlled by the radical entry and radical desorption. Both can be considered as monomolecular mechanisms of termination.

Additional information:

$M_{\mathrm{m,M}}$	=	100	g mol^{-1}	$M_{\mathrm{m,I}}$	=	164	g mol^{-1}
ϕ^*_{M}	=	0.5		ρ_{M}	=	0.94	kg L^{-1}
ρ_{Pol}	=	1.10	kg L^{-1}	ρ_{S}	=	1.00	kg L^{-1}
k_{d}	=	5.55×10^{-6}	s^{-1}	f	=	0.5	
k_{p}	=	715	L mol^{-1} s^{-1}	k_{t}	=	9.8×10^{6}	L mol^{-1} s^{-1}
d^0_{Pol}	=	50	nm				
k_{e}	=	1×10^{-7}	m s^{-1}	k_{des}	=	1×10^{-1}	s^{-1}
cmc	=	40×10^{-3}	mol L^{-1}	a_{E}	=	50	$\mathring{A}^2$
K_{E}	=	100	L mol^{-1}				

- You can consider the Initiator concentration constant over time.
- Assume the concentration of radicals in water is given by $R_W = \sqrt{\frac{2fk_dI_2}{k_t}}$
- You can consider the total volume of your suspension constant.