EXERCISES TO THE LECTURE POLYMER REACTION & COLLOID ENGINEERING

SERIES 5

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Cumulative Chain Length Distribution

Let us focus again on the polymerization system as already described in Series 2:

$$
\begin{aligned}
\mathrm{I}_2 &\xrightarrow{k_\mathrm{d}} 2\mathrm{R}_1 \\
\mathrm{R}_j + \mathrm{M} &\xrightarrow{k_\mathrm{p}} \mathrm{R}_{j+1} \\
\mathrm{R}_j + \mathrm{M} &\xrightarrow{k_\mathrm{fm}} \mathrm{R}_1 + \mathrm{P}_j \\
\mathrm{R}_i + \mathrm{R}_j &\xrightarrow{k_\mathrm{td}} \mathrm{P}_i + \mathrm{P}_j \\
\mathrm{R}_i + \mathrm{R}_j &\xrightarrow{k_\mathrm{tc}} \mathrm{P}_{i+j}
\end{aligned}
$$

There is again a 20 L batch reactor available to carry out the polymerization and you decide again to do the reaction as a solution polymerization using benzene as solvent. Moreover, you consider the same expressions in order to describe diffusion limitations:

$$
\begin{aligned}
k_\mathrm{p} &= \frac{1}{\frac{1}{k_{\mathrm{p},0}} + \frac{\exp(C_\eta w_\mathrm{p})}{k_{\mathrm{pD},0}}} \\
k_\mathrm{t} &= \frac{1}{\frac{1}{k_{\mathrm{t},0}} + \frac{\exp(C_\eta w_\mathrm{p})}{k_{\mathrm{tD},0}}} + C_\mathrm{RD} k_\mathrm{p} \left(1 - w_\mathrm{p}\right)
\end{aligned}
$$

where w_p is the weight fraction of the polymer in the reaction mixture. Finally, you define again the following ratios:

$$
\begin{aligned}
C_\mathrm{fm} &= \frac{k_\mathrm{fm}}{k_\mathrm{p}} \\
C_\mathrm{t} &= \frac{k_\mathrm{td}}{k_\mathrm{tc}}
\end{aligned}
$$

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a) Determine the entire cumulative number and weight CLD of the above described system using the following "model" parameter values:

$$\begin{aligned} M_0 &= 4.7 \quad \text{mol L}^{-1} \\ I_0 &= 6.0 \quad \text{mol L}^{-1} \\ k_{\text{p},0} &= 25 \quad \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

Plot them again at four different conversions ($X = 0.10,\ 0.40,\ 0.70,\ 0.90$). Compute the cumulative number average, $\overline{n}_{\text{N}}^{\text{c}}$ and weight average $\overline{n}_{\text{W}}^{\text{c}}$ of the CLD as well as the cumulative polydispersity index σ^{c} from the distributions and plot them versus conversion. Consider the case where disproportionation is the dominating termination step and no chain transfer to monomer occurs.

Let us now focus on the system using more realistic parameter values, i.e., the conditions considered in Series 2:

$$\begin{aligned} M_0 &= 4.7 \quad \text{mol L}^{-1} \\ w_{\text{I},0} &= 0.01 \\ k_{\text{p},0} &= 620 \quad \text{L mol}^{-1}\ \text{s}^{-1} \end{aligned}$$

Since much longer chains are produced in this case ($n \approx 10^4$ monomer units) it is not anymore convenient to compute the entire cumulative CLD (the resulting system of ODE's would consist of 10^4 equations!). Instead, we focus only on few properties of the CLD, the so-called moments.

Thus, calculate now the number ($\overline{n}_{\text{N}}^{\text{c}}$) and weight ($\overline{n}_{\text{W}}^{\text{c}}$) average of the cumulative CLD as well as the polydispersity index σ^{c} as a function of conversion, X for the "real" system using the moments of the distribution. Consider the following cases:

b) Termination by disproportionation dominates (i.e. $C_{\text{fm}} = 0$, $C_{\text{t}} = 1000$)

c) Termination by combination dominates (i.e. $C_{\text{fm}} = 0$, $C_{\text{t}} = 0.001$)

d) Termination by combination is negligible and chain transfer to monomer dominates (i.e. $C_{\text{fm}} = 0.01$, $C_{\text{t}} = 1000$)

e) In case of changing total volume,the gel effect could also be described by a dependency on the volume fraction of formed polymer. Which changes would you have to carry out in the program code, if the density of the formed polymer ρ_{P} would differ to the density of the monomer ρ_{M} used. Explain and state the necessary changes and formulas.

f) In almost every practical field engineers are facing all kinds of different populations. They are characterized by means of distributions and, together with this, by means of average measures of distributions, i.e., moments, moment ratios, ratios of moment ratios. Find examples for the moments of the orders (0 to 3), where the corresponding moment represents some physical property of a population. These order moments are all closely related to polymer science and play an important role in characterization of polymers. Do you know analytical methods applied for the characterization of polymers applying one of these moments?

Additional information:

$M_{\mathrm{m,M}}$	$=$	100	g mol^{-1}	$M_{\mathrm{m,I}}$	$=$	164	g mol^{-1}
$M_{\mathrm{m,S}}$	$=$	78	g mol^{-1}	ρ_{S}	$=$	0.88	kg L^{-1}
ρ_{M}	$=$	0.94	kg L^{-1}	f	$=$	0.5	
k_{d}	$=$	6.77×10^{-6}	s^{-1}	$k_{\mathrm{t,0}}$	$=$	9.2×10^{6}	L mol^{-1} s^{-1}
$k_{\mathrm{pD,0}}$	$=$	2×10^{11}	L mol^{-1} s^{-1}	$k_{\mathrm{tD,0}}$	$=$	5×10^{8}	L mol^{-1} s^{-1}
C_{η}	$=$	25		C_{RD}	$=$	180	

- Neglect the presence of the initiator when evaluating the initial solvent concentration as well as in the computation of the polymer weight fraction w_{p}. Note that this is reasonably done under "realistic" conditions and assumed for sake of simplicity in (a).

- Use a small initial amount of polymer for the numerical integration (i.e. $P(t=0) = 10^{-10}$ mol L^{-1}); otherwise there is a division by zero.

- Try to find an expression suitable for numerics to solve the cumulative CLD, averages and polydisperisty index. For this try to derive an ODE according to the example given for the moments (Equation 3.13 in the notes).