EXERCISES TO THE LECTURE POLYMER REACTION & COLLOID ENGINEERING

SERIES 6

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Copolymerization

The styrene(A)/MMA(B)-copolymerization is to be carried out in a 15-L batch reactor under bulk conditions at 65°C. In order to be prepared for the planned experiments you decide to make a few calculations first. In the literature you found values for the reactivity ratios which are $r_A = 0.52$ and $r_B = 0.46$, respectively. You decide to consider the following typical reaction steps of a free-radical copolymerization:

$$
\begin{aligned}
\mathrm{I}_2 &\xrightarrow{k_\mathrm{d}} 2\mathrm{I}^\bullet \\
\mathrm{I}^\bullet + \mathrm{A} &\xrightarrow{k_\mathrm{IA}} \mathrm{A}_1^\bullet \\
\mathrm{I}^\bullet + \mathrm{B} &\xrightarrow{k_\mathrm{IB}} \mathrm{B}_1^\bullet \\
\mathrm{A}_{m,n}^\bullet + \mathrm{A} &\xrightarrow{k_\mathrm{pAA}} \mathrm{A}_{m+1,n}^\bullet \\
\mathrm{A}_{m,n}^\bullet + \mathrm{B} &\xrightarrow{k_\mathrm{pAB}} \mathrm{B}_{m,n+1}^\bullet \\
\mathrm{B}_{m,n}^\bullet + \mathrm{A} &\xrightarrow{k_\mathrm{pBA}} \mathrm{A}_{m+1,n}^\bullet \\
\mathrm{B}_{m,n}^\bullet + \mathrm{B} &\xrightarrow{k_\mathrm{pBB}} \mathrm{B}_{m,n+1}^\bullet \\
\mathrm{A}_{m,n}^\bullet + \mathrm{A}_{r,q}^\bullet &\xrightarrow{k_\mathrm{tAA}} P_{m+r,n+q} \text{ or } P_{m,n} + P_{r,q} \\
\mathrm{A}_{m,n}^\bullet + \mathrm{B}_{r,q}^\bullet &\xrightarrow{k_\mathrm{tAB}} P_{m+r,n+q} \text{ or } P_{m,n} + P_{r,q} \\
\mathrm{B}_{m,n}^\bullet + \mathrm{B}_{r,q}^\bullet &\xrightarrow{k_\mathrm{tBB}} P_{m+r,n+q} \text{ or } P_{m,n} + P_{r,q}
\end{aligned}
$$

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Making good experience in the past you decide to use again the Buback-expression to describe glass and gel effect:

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

where w_{p} is the weight fraction of the polymer in the reaction mixture. Finally, you elect to carry out the following pre-calculation:

a) The determination of the instantaneous as well as the cumulative composition of the produced polymer chains as a function of the overall conversion. In addition, the computation of the instantaneous composition of the produced polymer chains as a function of monomer mixture composition. (**Hint:** To solve this part you only need the initial composition and the reactivity ratios.)

b) The evaluation of the evolution of the monomer concentrations versus time as well as the overall conversion versus time.

c) The calculation of the cumulative number average, $\overline{n}_{\mathrm{N}}^{\mathrm{c}}$ and weight average $\overline{n}_{\mathrm{W}}^{\mathrm{c}}$ of the CLD as well as the cumulative polydispersity index σ^{c} as a function of the overall conversion for the above described copolymerization system assuming that disproportionation is the dominating termination step.

Additional information:

$c_{\mathrm{A}}^{0} =$	3.5	mol/L	$w_{\mathrm{I}}^{0} =$	0.01	
$\rho_{\mathrm{A}} =$	0.90	kg/L	$\rho_{\mathrm{B}} =$	0.94	kg/L
$M_{\mathrm{m,A}} =$	104	g/mol	$M_{\mathrm{m,B}} =$	100	g/mol
$M_{\mathrm{m,I}} =$	164	g/mol	$k_{\mathrm{tAB}} =$	$\sqrt{k_{\mathrm{tAA}} k_{\mathrm{tBB}}}$	L/mol/s
$k_{\mathrm{d}} =$	6.77e-6	1/s	$f =$	0.5	
$k_{\mathrm{pAA}}^{0} =$	4.1e2	L/mol/s	$k_{\mathrm{tAA}}^{0} =$	2.4e7	L/mol/s
$k_{\mathrm{pA,D}}^{0} =$	2e11	L/mol/s	$k_{\mathrm{tA,D}}^{0} =$	5e8	L/mol/s
$C_{\eta,\mathrm{A}} =$	25		$C_{\mathrm{RD,A}} =$	180	
$k_{\mathrm{pBB}}^{0} =$	9.3e2	L/mol/s	$k_{\mathrm{tBB}}^{0} =$	9.2e6	L/mol/s
$k_{\mathrm{pB,D}}^{0} =$	2e11	L/mol/s	$k_{\mathrm{tB,D}}^{0} =$	5e8	L/mol/s
$C_{\eta,\mathrm{B}} =$	25		$C_{\mathrm{RD,B}} =$	180