

Chapter 2

Closed-Form Estimation of Minimum Reactive Polymer Domain Size for FRRPP Control

This chapter pertains to the derivation of the analytical expression for estimation of the minimum reactive polymer-rich domain size for the occurrence of a flat temperature profile in FRRPP systems, under quasi-steady-state conditions. The method assumes a cut-off value of $-1,000$ for $C\tilde{n}$, and it is based on temperature dependency of the product of the monomer and polymer composition in the polymer-rich domains. With the derived approximate equation, the resulting minimum polymer-rich domain sizes for FRRPP control are obtained for the PS–S–Ether and PMAA–MAA–Water systems. Finally, the resulting analytical expressions explain why asymptotic conversions in FRRPP systems can be relatively low if good radical trapping is realized in the system.

2.1 Derivation of Equations

Local monomer concentration $[M]$ and the polymer radical concentration $[P\cdot]$ can be compared to their base values ($[M]_0$ and $[P\cdot]_0$) through

$$[M] = [M]_0 + \Delta[M], \quad (2.1)$$

$$[P\cdot] = [P\cdot]_0 + \Delta[P\cdot]. \quad (2.2)$$

If x is the average degree of polymerization, then it should also be noted from a reactive component balance that

$$\Delta[M] = -x\Delta[P\cdot]. \quad (2.3)$$

For the propagation reaction rate, $R_p = k_p[M][P\cdot]$, that is to be used in the expression for $C\tilde{n}$, we obtain the expression for $[M][P\cdot]$ as

$$\begin{aligned}
[M][P\cdot] &= ([M]_0[P\cdot]_0 + \Delta[M])([P\cdot]_0 + \Delta[P\cdot]) = ([M]_0 - x\Delta[P\cdot])([P\cdot]_0 + \Delta[P\cdot]) \\
&= [P\cdot]_0[M]_0 + [M]_0\Delta[P\cdot] - x[P\cdot]_0\Delta[P\cdot] - x(\Delta[P\cdot])^2.
\end{aligned} \tag{2.4}$$

The last term of the right-hand side of eq. (2.4) could be neglected compared to the other terms because $\Delta[P\cdot] \ll [P\cdot]_0$; thus,

$$[M][P\cdot] = [P]_0[M]_0 + \Delta[P\cdot]([M]_0 - x[P\cdot]_0). \tag{2.5}$$

If $[P\cdot]$ is considered to vary only with the temperature and a linear dependence with temperature is invoked,

$$\Delta[P\cdot] \cong \left(\frac{d[P\cdot]}{dT} \right) (T - T_0). \tag{2.6}$$

Substituting the $\Delta[P\cdot]$ approximation from eq. (2.1.6) into eq. (2.1.5), we obtain

$$\begin{aligned}
[M][P\cdot] &= [P]_0[M]_0 + ([M]_0 - x[P\cdot]_0) \left(\frac{d[P\cdot]}{dT} \right) (T - T_0) \\
&= \left(\frac{d[P\cdot]}{dT} \right) \{ [M]_0 - x[P\cdot]_0 \} T - \left\{ [P\cdot]_0[M]_0 + \left(\frac{d[P\cdot]}{dT} \right) ([M]_0 - x[P\cdot]_0) T_0 \right\}.
\end{aligned} \tag{2.7}$$

If $[M][P\cdot] = a'T + b'$, then comparing with eq. (2.7),

$$a' = \left(\frac{d[P\cdot]}{dT} \right) \{ [M]_0 - x[P\cdot]_0 \}, \tag{2.8}$$

$$b' = [P\cdot]_0[M]_0 - a'T_0. \tag{2.9}$$

From the derivation in Sect. 1.1, the quantity $C\tilde{n}$ can be obtained as

$$C\tilde{n} = \Gamma \frac{a'b'T_0}{a'T_0 + b'}, \tag{2.10}$$

where

$$\Gamma = \frac{k_P(-\Delta H_P)r_0^2}{k} = \frac{k_{P0}\exp\left(-\frac{E_{Pa}}{RT_0}\right)r_0^2}{k}. \tag{2.11}$$

Simplification of eq. (2.10) leads to

$$C\tilde{n} = \frac{\Psi}{1 + \left(\frac{1}{\Omega-1}\right)}, \tag{2.12}$$

where

$$\Psi = a'\Gamma T_0 \quad (2.13)$$

and

$$\Omega = \frac{[P\cdot]_0[M]_0}{a'T_0} < 1. \quad (2.14)$$

From dimensional analysis,

$$[P\cdot]_0 = \left(\frac{\rho_{\text{Soln}}}{\text{MW}_{\text{Polymer}}} \right) f_P X_P, \quad [M]_0 = \left(\frac{\rho_{\text{Soln}}}{\text{MW}_{\text{Monomer}}} \right) X_M, \quad (2.15)$$

where ρ_{Soln} is the density of the reactive solution environment; $\text{MW}_{\text{Polymer}}$ and $\text{MW}_{\text{Monomer}}$ are the molecular weights of the polymer and monomer, respectively; and f_P is the fraction polymer radical from all polymer species (live and dead polymer molecules). Thus,

$$\Omega = \left(\frac{\rho_{\text{Soln}}^2}{\text{MW}_{\text{Monomer}} \text{MW}_{\text{Polymer}} a' T_0} \right) f_P X_M X_P. \quad (2.16)$$

From Eqs. (1.10) and (1.11), the polymer-rich domain size can be obtained as

$$r_0 = \sqrt{\frac{C\tilde{n}}{T_0\alpha_0} \left(1 + \frac{1}{\Omega - 1} \right)}, \quad (2.17)$$

where the quantity α_0 is defined in Eq. (1.18). If the cutoff $C\tilde{n} \leq -1,000$ for flat temperature profile FRRPP behavior applied to quasi-steady-state conditions, then this corresponds to the cutoff r_0 as

$$r_0 \geq \sqrt{\frac{1,000}{T_0\alpha_0} \left(\frac{1}{1 - \Omega} - 1 \right)}. \quad (2.18)$$

2.2 Results and Discussion

Applying the values of T_0 , α_0 , and Ω for the PS–S–Ether and PMAA–MAA–Water system, the cut-off values of r_0 are obtained for flat temperature profile FRRPP behavior (Table 2.1).

Table 2.1 Approximate predictions of the cut-off values of r_0 for the PS–S–Ether and PMAA–MAA–Water systems, based on the derivation in eqs. (2.1)–(2.16)

System	T_0 , K	α_0 , cm ⁻²	Ω	r_0 , cm
PS–S–Ether	353	1.700×10^8	0.00261–0.00278	0.000124–0.000128
			($f_p = 0.8$ –0.85)	($f_p = 0.8$ –0.85)
PMAA–MAA–Water	353	3.44×10^3	6.287×10^{-6} – 6.287×10^{-5}	0.00135–0.00427
			($f_p = 0.01$ –0.1)	($f_p = 0.01$ –0.1)

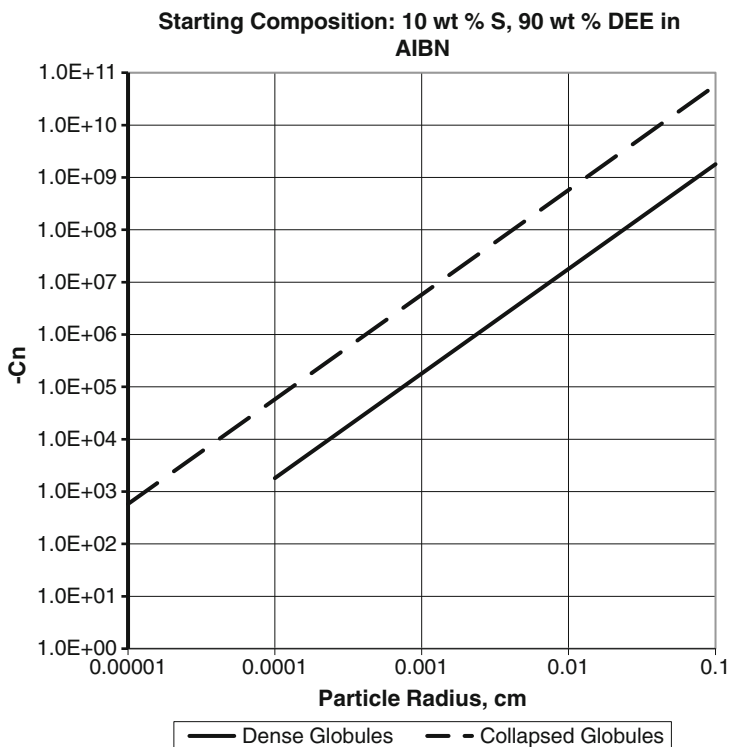


Fig. 2.1 Cutoff off reactive domain size for the PS–S–Ether FRRPP system at 80°C, based on $C\bar{n} < -1,000$ (Discrepancy between this plot and Fig. 2.5.2 of Caneba (2010) is also due to an arithmetic error. Corrected values of α_0 and β_0 are 1.700×10^8 and -1.121×10^8 cm⁻² for collapsed globules, respectively; also respective values are 8.10×10^4 and -5.34×10^4 cm⁻² for dense globules). The value of $f_p = 0.80$. Note that lines for $f_p = 0.85$ has been found to be almost the same for corresponding lines at $f_p = 0.80$

It is evident that the predictions of eq. (2.18) provide conservative values for the cutoff r_0 based on results in Sect. 2.5 of Caneba (2010) for PS–S–Ether system (which has been modified to Fig. 2.1). For the PMAA–MAA–Water system, Chap. 1 of this monograph indicates that the results in Table 2.1 are approximate.

The reason why only approximate values were obtained is the use of approximations in the above-mentioned derivations of Ω [eq. (2.16)] and r_0 [eq. (2.18)]. Still, these expressions are very useful in estimation of values of r_0 for FRRPP behavior.

Equation (2.8) can be further developed to yield a result that explains some of the critical experimental observation in FRRPP systems. An assumption is made here in which the polymer radical fraction, f_p , is a constant, as it was observed in both PS–S–Ether system (Figs. 2.3.14 and 2.3.15 of Caneba 2010) and also in the PMAA–MAA–Water system (Fig. 2.3.22 of Caneba 2010). With the use of eq. (2.15) and the fact that $x = MW_{\text{Polymer}}/MW_{\text{Monomer}}$,

$$a' = \frac{f_p \rho_{\text{Soln}}^2}{MW_{\text{Polymer}} MW_{\text{Monomer}}} (X_M - f_p X_P) \frac{dX_P}{dT} > 0. \quad (2.19)$$

Based on initial phase equilibrium conditions, $a' > 0$, or

$$X_M - f_p X_P > 0. \quad (2.20)$$

The implication of eq. (2.20) for FRRPP behavior is that it happens when the monomer concentration is relatively large compared to the polymer concentration. For example, if the system converts all polymer species into radicals ($f_p = 1$), then the asymptotic conversion of polymerization may not be more than 50%. This explains the relatively low asymptotic conversions for some FRRPP systems, such as the PS–S–Ether system at 80°C (23–30%). Note that the relatively high value of f_p (0.80–0.85) for this system forces the asymptotic conversion to be relatively low for FRRPP behavior, based on eq. (2.20). In this case, the cut-off reactive domain size is obtained and shown in Fig. 2.1 for $f_p = 0.80$, based on $C\bar{n} < -1,000$.

Based on Fig. 2.1, reactive domains of the PS–S–Ether system at 350 μm in the reactor are definitely going to fall into the strict FRRPP category, if it is under quasi-steady-state conditions. However, if emulsification of these domains is done to reduce domain sizes to 0.1–1 μm , then these domains could start to exhibit less flat temperature profiles.

If a relatively high asymptotic conversion is obtained, such as the PMAA–MAA–Water system at 80°C or 90°C (80–90%), a relatively low polymer radical fraction value (f_p) would have to happen, as it actually occurs to be in the order of 0.03 for such a system (Sect. 1.1).

The above-mentioned analysis is based on local temperature variations that occur in FRRPP systems that do not employ a dispersing agent for the polymer-rich domains. If an emulsifier is used to force the polymer-rich domains into micron or even submicron scales, domain temperatures may not be flat and they approach those of the dispersing fluid. The implication of this kind of situation will be discussed in the next chapters.

2.3 Nomenclature

2.3.1 *Alphabets*

2.3.1.1 Upper Case

MW	Molecular weight, g/mol or Daltons
R	Universal gas constant, J/(mol K)
T	Absolute temperature, K
X	Weight fraction, dimensionless

2.3.1.2 Lower Case

a'	Defined in eq. (2.8)
b'	Defined in eq. (2.9)
k	Thermal conductivity of the reaction fluid
r	Radial distance, m or cm
x	Average degree of polymerization of the polymer

2.3.2 *Subscripts*

a	Pertains to activation energy [eq. (2.11)]
M	Pertains to monomer in eqs. (2.15), (2.16), (2.19), and (2.20)
Monomer	Pertains to monomer
P	Pertains to polymer-rich phase in eqs. (2.15), (2.16), (2.19), and (2.20)
Polymer	Pertains to polymer
Soln	Pertains to overall solution

2.3.3 *Superscripts*

None

2.3.4 *Greek Symbols*

Γ	Defined in eq. (2.11), dimensionless
Ψ	Defined in eq. (2.13), dimensionless
Ω	Defined in eq. (2.14), dimensionless

2.3.5 Other Symbols

a'	Defined in Eq. (2.8)
b'	Defined in Eq. (2.9)
α_0	Defined in Eq. (1.18), cm^{-2} or m^{-2}
β_0	Defined in Eq. (1.19), cm^{-2} or m^{-2}
$C\bar{n}$	Defined in Eq. (1.13), dimensionless
Δ	Change operator (Final minus Initial)
E_P	Activation energy for propagation reaction, used in Eq. (2.11), J/(mol K)
f_P	Polymer radical fraction, dimensionless
ΔH_P	Heat of polymerization, J/mol
k'_0	Defined in Eq. (1.14)
k_P	Propagation rate coefficient, l/(mol s)
MW	Molecular weight, Daltons or g/mol
$[M]$	Monomer concentration, mol/l
$[M]_0$	Initial monomer concentration, mol/l
ρ	Density, g/cm^3 or kg/m^3
r_0	Particle radius, cm or m
$[P\cdot]$	Polymer radical concentration, mol/l
$[P\cdot]_0$	Initial polymer radical concentration, mol/l
T_0	Initial temperature, K

Reference

Caneba GT (2010) Free-radical retrograde-precipitation polymerization (FRRPP): novel concept, processes, materials, and energy aspects. Springer, Heidelberg. ISBN 978-3-642-03024-6

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