Chapter Six Soft condensed matter
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6.1. In a certain chemical cross-linking reaction involving a monomer that can react at three sites, the degree of reaction f obeys the second-order rate law

$$\frac{df}{dt} = k(1-f)^2 \tag{1}$$

where the rate constant k has the value $4 \times 10^{-4} s^{-1}$. Use the Flory_Stochmayer theory to calculate

a. the times at which the gel point is reached,

$$(1) \rightarrow \frac{df}{dt} = k(1-f)^2 \rightarrow \frac{df}{(1-f)^2} = kdt$$

$$\int_0^f \frac{df'}{(1-f')^2} = \int_0^t kdt' \rightarrow \frac{1}{1-f} - 1 = kt$$

$$\frac{f}{1-f} = kt \tag{2}$$

$$(6.4) \rightarrow f_c = \frac{1}{z-1} = \frac{1}{3-1} = \frac{1}{2}$$

$$t_c = \frac{1}{k}(2-1) = \frac{1}{k} = \frac{1}{4} \times 10^4 s = 2500s$$

b. the time after which three quarters of monomers have been polymerized,

$$f = \frac{3}{4}, (2) \rightarrow 3 = kt \rightarrow t = \frac{3}{k} = \frac{3}{4} \times 10^4 s$$

$$t = 7500s$$

c. the time after which three quarters of monomers form part of the infinite network.

$$(6.7) \rightarrow P = f(1-Q^3), f > f_c \rightarrow P = f(1-(\frac{1-f}{f})^3)$$

$$\frac{3}{4} = f(1-(\frac{1-f}{f})^3)$$

roots:

$$f_1 = 0.77039, f_2 = 0.55230 - 0.58650i, f_3 = 0.55230 + 0.58650i$$

$$(2) \rightarrow kt = \frac{0.77039}{1-0.77039} = 3.35521101$$

$$t = \frac{1}{k}3.35521101 = 8388.027s$$

6.2. In an experiment to test the application of the theory of peculation to gelation, the gel fraction is determined when the fractional extent of reaction is a small degree Δf larger than its value at the gel point.

a. Is the value of gel fraction at a fractional extent of reaction $\Delta f/2$ larger or smaller when predicated by peculation theory than the value predicted by Flory_Stochmayer theory?

b.By what factor do the two prediction differ?

we know for classical peculation theory the gel fraction can be expanded:

$$(6.9) \rightarrow \frac{P}{f} = 3(f - f_c) + O(f - f_c)^3$$

Considering the leading order the relation is linear and therefore:

$$\Delta f \rightarrow \frac{\Delta f}{2} \Rightarrow \frac{P}{f} \rightarrow \frac{P}{f} \times 0.5$$

By contrast, Monte Carlo Simulation of bond peculation in 3D gives:

$$\frac{P}{f} = (f - f_c)^{0.41}$$

therefore

$$\Delta f \rightarrow \frac{\Delta f}{2} \Rightarrow \frac{P}{f} \rightarrow \frac{P}{f} \times 0.7526$$

the value predicted by Flory_Stochmayer theory is smaller.