CHEMISTRY LETTERS, pp. 1083-1084, 1989.

On the Flory-Stockmayer Model of Gelation Accompanied by the Intra Particle Crosslinking Reaction

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The approximative particle size distribution function in the crosslinking reaction according to the Flory-Stockmayer model involving intra particle crosslinking is derived by the modification of the general solution obtained by Leyvraz and Tschudi.

The general solution of the Flory-Stockmayer equation (1)[1] was derived by Leyvraz and Tschudi (2).[2] The conditions of the macrogelation, sol and gel fractions after gelation etc. can be obtained automatically by this excellent treatment:

$$\frac{dc(j,t)}{dt} = \sum_{\substack{g+h=j \\ g>h}} R(g,h)c(g,t)c(h,t) - \sum_{i=1}^{\infty} R(i,j)c(i,t)c(j,t) \qquad (1)$$

$$R(i,j)=(Ai+B)(Aj+B)=\kappa(ai+b)(aj+b)$$

$$c(j,\tau) = \frac{j^{j-3}}{(j-1)!}\tau^{j-1}e^{-j\tau}, \quad \tau=\kappa(a+b)^2 \quad (\tau<1) \qquad (2)$$

$$= \frac{j^{j-3}e^{-j}}{(j-1)!}\frac{1}{\tau} \qquad (\tau\geqslant 1)$$

where c(j,t) is the concentration of the particles composed of j pre-polymers (j-mer) and R(i,j) is the rate constant.

Here we imagine a pre-polymer with f reactive groups. The polymers join together with these reactive groups. The number of the reactive groups in j-mer is $[(f-2)j+2]$, if the intra particle reaction does not take place. In the Flory-Stockmayer model, a, b correspond to (f-2) and 2 respectively, and reactive groups are consumed only by the inter particles reaction.

In the actual cases, the intra particle crosslinking can not be ignored or is a main reaction. Then it is worthy to derive the solution of the Flory-Stockmayer equation involving the intra particle crosslinking. Let's set up three approximations: 1) $f\gg 2$, then $[(f-2)j+2]\simeq fj$, a=f, and b=0. 2) The rate of the intra particle crosslinking is independent to the particle size. 3) The reactive groups are consumed mainly by intra particle crosslinking.

Then the functionality of j-mer at time t is $f=f_0\xi(t)\cdot j$ (f_0 is f at t, and $1-\xi(t)$ is the conversion of the reactive groups at time t). As a result, the rate of the crosslinking between i-mer and j-mer becomes $\kappa f_0^2\,\xi(t)^2\cdot i\cdot j\cdot c(j)c(k)$. Let's consider two reactions:

$$\text{i-mer} + \text{j-mer} \xrightarrow{\text{rate}(i,j)} \text{(i+j)-mer:}\quad \text{rate}(i,j)=\kappa f_0^2\xi(t)^2 i\cdot j\cdot c(j)c(k) \qquad (3)$$

$$\text{r-mer} + \text{s-mer} \xrightarrow{\text{rate}(r,s)} \text{(r+s)-mer:}\quad \text{rate}(r,s)=\kappa f_0^2\xi(t)^2 r\cdot s\cdot c(r)c(k) \qquad (4)$$

The ratio rate(i,j)/rate(r,s) is $i\cdot jc(i)c(j)/r\cdot sc(r)c(s)$. Then the ratios of any two reaction rates become independent to $\xi(t)$. Generally it is clear that if functionality f is far larger than 2, rate(j,k)/rate(r,s) becomes approximately independent to f itself. Under this condition, the size distribution functions in two cases (without and with intra crosslinking reaction) are able to coincide by only a change of time scale. Then a problem is to find out the relation between $\xi(t)$ and the rate of the inter particles crosslinking.

Now, let's suppose that the concentration of j-mer c(j) is expressed as $c(j,\tau(t))$, when the intra particle crosslinking is involved. Then:

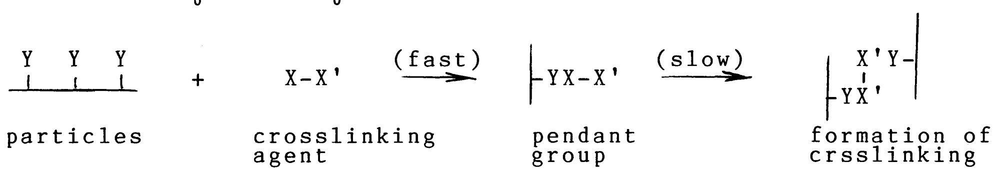
$$\frac{dc(j,\tau(t))}{dt} = \sum R'(g,h)c(g,\tau)c(h,\tau) - \sum R'(i,j)c(i,\tau)c(j,\tau)$$

$$= \xi^2\cdot\frac{dc(j,\tau)}{d\tau}\ ,\qquad R' = \kappa f_0^2\xi(t)^2\cdot i\cdot j \qquad (5)$$

As a result:

$$\frac{d\tau(t)}{dt} = \xi(t)^2 \qquad (6)$$

For an example, in the following crosslinking reaction by two steps (Schme 1) (concn. of Y $\gg$ concn. of X and X'), the functionality f(t) in pre-polymer is approximately: $f(t)=f_0\xi(t) = [X']_0\exp(-\kappa'[Y]_0 t)$. When $\tau(t)<1$ in all t, that is to say $1>[X']_0{}^2/8\kappa'[Y]_0$, gelation does not occur.



Scheme 1.

References
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2) F.Leyvraz and H.R.Tschudi, J. Phys. A: Math. Gen., 14, 3389-3405 (1981)

(Received March 24, 1989)