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Acrylate Network Formation by Free-Radical Polymerization Modeled Using Random Graphs

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Acrylate network modeling using random graphs - Supporting information

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1. Derivation of $\dot{c}_r$, $\dot{c}_v$, $\dot{c}_c$ and $[\dot{M}_2]$

The following section provides detailed derivations of the PBEs for the total concentration of radicals $\dot{c}_r$, FPDBs $\dot{c}_v$, crosslinks $\dot{c}_c$ and reacted monomer units $\dot{c}_s = 1 - [\dot{M}_2]$ in the diacrylate system. The expressions equal the first moments of the time derivative of the probability mass function $\dot{f}_{s,v,z}$, which was defined in the paper as

$$\begin{aligned}
\dot{f}_{s,v,r} =& \phi_i + \phi_p + \phi_c + \phi_{td} + \phi_{tc} \\
=& 2k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big) \\
&+ 2k_p r[M_2](f_{s-1,v-1,r} - f_{s,v,r}) \\
&+ k_p \sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - k_p(c_r v + c_v r)f_{s,v,r} \\
&+ 2k_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) \\
&+ k_{tc} \sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - 2k_{tc}c_r r f_{s,v,r}.
\end{aligned} \tag{1}$$

Thus, the PBEs can be written as

$$\dot{c}_r = \sum_{(s,v,r)=(0,0,0)}^{\infty} r\dot{f}_{s,v,r}, \tag{2}$$

$$\dot{c}_v = \sum_{(s,v,r)=(0,0,0)}^{\infty} v\dot{f}_{s,v,r}, \tag{3}$$

$$\dot{c}_c = \sum_{(s,v,r)=(0,0,0)}^{\infty} c\dot{f}_{s,v,r} = \sum_{(s,v,r)=(0,0,0)}^{\infty} (s-v)\dot{f}_{s,v,r}, \tag{4}$$

$$[\dot{M}_2] = -\dot{c}_s = -\sum_{(s,v,r)=(0,0,0)}^{\infty} s\dot{f}_{s,v,r}. \tag{5}$$

1.1. Derivation of $\dot{c}_r$

The derivation of the PBE for the concentration of radicals, defined as

$$\begin{aligned}
\dot{c}_r = &\sum_{(s,v,r)=(0,0,0)}^{\infty} r\Big[k_i 2[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big)\Big] \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} rk_p r 2[M_2](f_{s-1,v-1,r} - f_{s,v,r}) \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} rk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'}(c_r v + c_v r)f_{s,v,r}\Big] \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} 2rk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} rk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - 2c_r rf_{s,v,r}\Big],
\end{aligned} \tag{6}$$

is split into five separate calculations, corresponding to the five contributing reactions:

1. Initiation

$$\sum_{(s,v,r)=(0,0,0)}^{\infty} r\Big[k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big)\Big] =$$

$$\begin{aligned}
&= 2k_i[M_2][I] + k_i[I]\Big[\sum_{(01-1)}^{\infty}(r+1)vf_{s,v,r} - \sum_{(0,0,0)}^{\infty} rvf_{s,v,r}\Big] \\
&= 2k_i[M_2][I] + k_i[I]\Big[\sum_{(0,0,0)}^{\infty}(r+1)vf_{s,v,r} - \sum_{(0,0,0)}^{\infty} rvf_{s,v,r}\Big] \\
&= 2k_i[M_2][I] + k_i[I]\sum_{(0,0,0)}^{\infty} vf_{s,v,r} \\
&= 2k_i[M_2][I] + k_i[I]c_v.
\end{aligned} \tag{7}$$

2. Propagation

$$\sum_{(s,v,r)=(0,0,0)}^{\infty} 2r^2k_p[M_2](f_{s-1,v-1,r} - f_{s,v,r}) =$$

$$\begin{aligned}
&= 2k_p[M_2]\Big[\sum_{(-1-10)}^{\infty} r^2 f_{s,v,r} - \sum_{(0,0,0)}^{\infty} r^2 f_{s,v,r}\Big] \\
&= 2k_p[M_2]\Big[\sum_{(0,0,0)}^{\infty} r^2 f_{s,v,r} - \sum_{(0,0,0)}^{\infty} r^2 f_{s,v,r}\Big] = 0.
\end{aligned} \tag{8}$$

3. Crosslinking

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} rk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - (c_r v + c_v r)f_{s,v,r}\Big] = \\
&= \sum_{(0,0,0)}^{\infty} rk_p\Big[\Big(rf_{s,v,r} * (v+1)f_{s,v+1,r}\Big)(c_r v + c_v r)f_{s,v,r}\Big] \\
&= \sum_{(0,0,0)}^{\infty} rk_p\Big[T_{010}\Big(rf_{s,v,r} * vf_{s,v,r}\Big) - (c_r v + c_v r)f_{s,v,r}\Big],
\end{aligned} \tag{9}$$

with T_{010} denoting a shift by 1 in the v-coordinate. To solve this equation in an elegant way, we introduce the generating function $F(x,y,z)$ of $f_{s,v,r}$ with

$$F(x,y,z) = \sum_{s,v,r}^{\infty} f_{s,v,r}x^s y^v z^r. \tag{10}$$

The most important properties of generating functions are discussed in the content of the paper.

The first moments of $f_{s,v,r}$ can now be written as

$$\begin{aligned} c_s &= \sum_{s,v,r}^{\infty} s f_{s,v,r} x^s y^v z^r \Big|_{x=y=z=1} = F_x(1,1,1), \\ c_v &= \sum_{s,v,r}^{\infty} v f_{s,v,r} x^s y^v z^r \Big|_{x=y=z=1} = F_y(1,1,1), \\ c_r &= \sum_{s,v,r}^{\infty} r f_{s,v,r} x^s y^v z^r \Big|_{x=y=z=1} = F_z(1,1,1), \end{aligned} \tag{11}$$

with $F_x(1,1,1) = \frac{\partial F(x,y,z)}{\partial x}|_{x=y=z=1}$, $F_y(1,1,1) = \frac{\partial F(x,y,z)}{\partial y}|_{x=y=z=1}$ and $F_z(1,1,1) = \frac{\partial F(x,y,z)}{\partial z}|_{x=y=z=1}$ denoting the partial derivatives of $F(x,y,z)$ evaluated at $(x,y,z) = (1,1,1)$.

In the domain of generating functions, a shift in the dimensions of $f_{s,v,r}$, e.g. to $f_{s,v,r+1}$ by applying T_{001} on $f_{s,v,r}$, translates to

$$\begin{aligned} \mathcal{F}(T_{001} f_{s,v,r}) &= \sum_{s,v,r}^{\infty} f_{s,v,r+1} x^s y^v z^r \\ &= \frac{1}{z} \sum_{s,v,r}^{\infty} f_{s,v,r+1} x^s y^v z^{r+1} \\ &= \frac{1}{z} \mathcal{F}(f_{s,v,r}), \end{aligned} \tag{12}$$

with $\mathcal{F}$ denoting the transformation to the domain of generating functions. Furthermore, the generating function of a convolution of two functions $f(s)$ and $g(s)$ is given by the multiplication of their generating functions $F(x)$ and $G(x)$,

$$\mathcal{F}\big((f * g)(s)\big) = F(x)G(x). \tag{13}$$

With these tools, Eq. (9) can be written as

$$
\begin{aligned}
& k_p\Big[z(\frac{1}{y}(zF_z yF_y))_z - z(F_z(1,1,1)yF_y + F_y(1,1,1)zF_z)_z\Big]|_{x=y=z=1} = \\
& = k_p\Big[\frac{1}{y}z(zF_z yF_y)_z - z(F_z(1,1,1)yF_{yz} + F_y(1,1,1)F_z + F_y(1,1,1)zF_{zz})\Big]|_{x=y=z=1} \\
& = k_p\Big[\frac{1}{y}z(F_z yF_y + zF_{zz}yF_y + zF_z yF_{yz}) \\
& \quad - z(F_z(1,1,1)yF_{yz} + F_y(1,1,1)F_z + F_y(1,1,1)zF_{zz})\Big]|_{x=y=z=1} \\
& = k_p\Big[F_z(1,1,1)F_y(1,1,1) + F_{zz}(1,1,1)F_y(1,1,1) + F_z(1,1,1)F_{yz}(1,1,1) \\
& \quad - F_z(1,1,1)F_{yz}(1,1,1) - F_y(1,1,1)F_z(1,1,1) - F_y(1,1,1)F_{zz}(1,1,1)\Big] \\
& = 0.
\end{aligned}
\tag{14}
$$

For reasons of readability, the explicit dependency on (x, y, z) of the partial derivatives of the generating function $F(x, y, z)$ is omitted.

4. Termination by disproportionation

$$
\begin{aligned}
\sum_{(s,v,r)=(0,0,0)}^{\infty} & 2rk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) = \\
& = 2k_{td}c_r\Big[\sum_{(0,0,0)}^{\infty} r(r+1)f_{s,v,r+1} - \sum_{(0,0,0)}^{\infty} r^2 f_{s,v,r}\Big] \\
& = 2k_{td}c_r\Big[\sum_{(0,0,1)}^{\infty} (r-1)rf_{s,v,r} - \sum_{(0,0,0)}^{\infty} r^2 f_{s,v,r}\Big] \\
& = -2k_{td}c_r^2.
\end{aligned}
\tag{15}
$$

5. Termination by recombination

$$
\begin{aligned}
\sum_{(s,v,r)=(0,0,0)}^{\infty} rk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - c_r r f_{s,v,r}\Big] = \\
&= \sum_{(s,v,r)=(0,0,0)}^{\infty} rk_{tc}\Big[((r+1)f_{s,v,r+1} * (r+1)f_{s,v,r+1}) - 2c_r r f_{s,v,r}\Big] \\
&= k_{tc} \sum_{(s,v,r)=(0,0,0)}^{\infty} \Big[rT_{0,0,2}(rf_{s,v,r} * rf_{s,v,r}) - 2c_r r^2 f_{s,v,r}\Big] \\
&= k_{tc}\Big[z(\frac{1}{z^2}(zF_z zF_z))_z - 2F_z(1,1,1)z(zF_z)_z\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[z(F_z^2)_z - 2F_z(1,1,1)(zF_z + z^2F_{zz})\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[2zF_{zz}F_z - 2F_z(1,1,1)(zF_z + z^2F_{zz})\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[2F_{zz}(1,1,1)F_z(1,1,1) - 2F_z(1,1,1)(F_z(1,1,1) + F_{zz}(1,1,1))\Big] \\
&= -2k_{tc}F_z(1,1,1)F_z(1,1,1) \\
&= -2k_{tc}c_r^2.
\end{aligned}
\tag{16}
$$

The summation over all five terms gives the PBE for the concentration of radicals

$$\dot{c}_r = k_i(2[M_2] + c_v)[I] - 2(k_{td} + k_{tc})c_r^2. \tag{17}$$

The derivation of the PBE for the concentration of the FPDBs $\dot{c}_v$ and reacted monomer units $\dot{c}_s$ is accomplished analogously.

1.2. Derivation of $\dot{c}_v$

The PBE for the concentration of FPDBs defined by Eq. (3), is obtained by evaluation of the expression

$$\begin{aligned}
\dot{c}_v = &\sum_{(s,v,r)=(0,0,0)}^{\infty} v\Big[k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big)\Big] \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} vk_p r[M_2](f_{s-1,v-1,r} - f_{s,v,r}) \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} vk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - (c_r v + c_v r)f_{s,v,r}\Big] \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} 2vk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) \\
&+ \sum_{(s,v,r)=(0,0,0)}^{\infty} vk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - 2c_r r f_{s,v,r}\Big],
\end{aligned} \tag{18}$$

which is done in five steps, again treating the contributing reactions one by one:

1. Initiation

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} v\Big[k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big)\Big] = \\
&\quad = 2k_i[M_2][I] + k_i[I]\Big[\sum_{(0,0,0)}^{\infty} v(v+1)f_{s,v+1,r-1} - \sum_{(0,0,0)}^{\infty} v^2 f_{s,v,r}\Big] \\
&\quad = 2k_i[M_2][I] + k_i[I]\Big[\sum_{(0,1,-1)}^{\infty} (v-1)vf_{s,v,r} - \sum_{(0,0,0)}^{\infty} v^2 f_{s,v,r}\Big] \\
&\quad = 2k_i[M_2][I] - k_i[I]\sum_{(0,0,0)}^{\infty} vf_{s,v,r} \\
&\quad = 2k_i[M_2][I] - k_i[I]c_v.
\end{aligned} \tag{19}$$

2. Propagation

$$\begin{aligned}\sum_{(s,v,r)=(0,0,0)}^{\infty} & 2vrk_p[M_2](f_{s-1,v-1,r} - f_{s,v,r}) = \\ &= 2k_p[M_2]\Big[\sum_{(0,0,0)}^{\infty} vrf_{s-1,v-1,r} - \sum_{(0,0,0)}^{\infty} vrf_{s,v,r}\Big] \\ &= 2k_p[M_2]\Big[\sum_{(-1,-1,0)}^{\infty} (v+1)rf_{s,v,r} - \sum_{(0,0,0)}^{\infty} vrf_{s,v,r}\Big] \\ &= 2k_p[M_2]c_r.\end{aligned} \tag{20}$$

3. Crosslinking

$$\begin{aligned}\sum_{(s,v,r)=(0,0,0)}^{\infty} & vk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - (c_r v + c_v r)f_{s,v,r}\Big] = \\ &= \sum_{(0,0,0)}^{\infty} vk_p\Big[\Big(rf_{s,v,r} * (v+1)f_{s,v+1,r}\Big) - (c_r v + c_v r)f_{s,v,r}\Big] \\ &= \sum_{(0,0,0)}^{\infty} vk_p\Big[T_{010}\Big(rf_{s,v,r} * vf_{s,v,r}\Big) - (c_r v + c_v r)f_{s,v,r}\Big], \\ &= k_p\Big[y(\frac{1}{y}(zF_z yF_y))_y - y(F_z(1,1,1)yF_y + F_y(1,1,1)zF_z)_y\Big]|_{x=y=z=1} = \\ &= k_p\Big[y(zF_zF_y)_y - y\big(F_z(1,1,1)F_y + F_z(1,1,1)yF_{yy} + F_y(1,1,1)zF_{zy}\big)\Big]|_{x=y=z=1} \\ &= k_p\Big[y(zF_{zy}F_y + zF_z yF_{yy}) \\ &\quad - y\big(F_z(1,1,1)F_y + F_z(1,1,1)yF_{yy} + F_y(1,1,1)zF_{zy}\big)\Big]|_{x=y=z=1} \\ &= k_p\Big[(F_{zy}(1,1,1)F_y(1,1,1) + F_z(1,1,1)F_{yy}(1,1,1)) \\ &\quad - (F_z(1,1,1)F_y(1,1,1) + F_z(1,1,1)F_{yy}(1,1,1) + F_y(1,1,1)F_{zy}(1,1,1))\Big] \\ &= -F_z(1,1,1)F_y(1,1,1) \\ &= -k_p c_r c_v.\end{aligned} \tag{21}$$

4. Termination by disproportionation

$$\sum_{(s,v,r)=(0,0,0)}^{\infty} 2vk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) =$$
$$= 2k_{td}c_r\Big[\sum_{(0,0,0)}^{\infty} v(r+1)f_{s,v,r+1} - \sum_{(0,0,0)}^{\infty} vrf_{s,v,r}\Big] \tag{22}$$
$$= 2k_{td}c_r\Big[\sum_{(0,0,1)}^{\infty} vrf_{s,v,r} - \sum_{(0,0,0)}^{\infty} vrf_{s,v,r}\Big] = 0.$$

5. Termination by recombination

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} vk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - c_rrf_{s,v,r}\Big] = \\
&= \sum_{(s,v,r)=(0,0,0)}^{\infty} vk_{tc}\Big[\big((r+1)f_{s,v,r+1} * (r+1)f_{s,v,r+1}\big) - 2c_rrf_{s,v,r}\Big] \\
&= k_{tc}\sum_{(s,v,r)=(0,0,0)}^{\infty}\Big[vT_{002}(rf_{s,v,r} * rf_{s,v,r}) - 2c_rvrf_{s,v,r}\Big] \\
&= k_{tc}\Big[y\big(\frac{1}{z^2}(zF_zzF_z)\big)_y - 2F_z(1,1,1)y(zF_z)_y\Big]\Big|_{x=y=z=1} \\
&= k_{tc}\Big[y(F_z^2)_y - 2F_z(1,1,1)yzF_{zy}\Big]\Big|_{x=y=z=1} \\
&= k_{tc}\Big[2yF_{zy}F_z - 2yzF_z(1,1,1)F_{zy}\Big]\Big|_{x=y=z=1} \\
&= k_{tc}\Big[2F_{zy}(1,1,1)F_z(1,1,1) - 2F_z(1,1,1)F_{zy}(1,1,1)\Big] = 0.
\end{aligned} \tag{23}$$

The PBE for the concentration of FPDBs is then given by the summation of all five terms,

$$\dot{c}_v = k_i(2[M_2] - c_v)[I] + 2k_p[M_2]c_r - k_pc_rc_v. \tag{24}$$

1.3. Derivation of $\dot{c}_c$ and $[\dot{M}_2]$

As stated in Eq. (4) and (5), the PBEs for the concentration of crosslinks $\dot{c}_c$ and the unreacted monomers $[\dot{M}_2]$ are given by

$$\begin{aligned}
\dot{c}_c &= \dot{c}_s - \dot{c}_v, \\
[\dot{M}_2] &= -\dot{c}_s.
\end{aligned} \tag{25}$$

Therefore, the PBE for the concentration of reacted monomer units $\dot{c}_s$ needs to be calculated by

$$\begin{aligned}
\dot{c}_s = & \sum_{(s,v,r)=(0,0,0)}^{\infty} s\Big[k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\Big((v+1)f_{s,v+1,r-1} - vf_{s,v,r}\Big)\Big] \\
& + \sum_{(s,v,r)=(0,0,0)}^{\infty} sk_p r[M_2](f_{s-1,v-1,r} - f_{s,v,r}) \\
& + \sum_{(s,v,r)=(0,0,0)}^{\infty} sk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - (c_r v + c_v r)f_{s,v,r}\Big] \\
& + \sum_{(s,v,r)=(0,0,0)}^{\infty} 2sk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) \\
& + \sum_{(s,v,r)=(0,0,0)}^{\infty} sk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - 2c_r rf_{s,v,r}\Big].
\end{aligned} \tag{26}$$

As in the previous sections, the expression is separated into its five terms, which correspond to the five reactions:

1. Initiation

$$\begin{aligned}
& \sum_{(s,v,r)=(0,0,0)}^{\infty} s\Big[k_i[M_2][I]\delta_{s-1,v-1,r-1} + k_i[I]\big[(v+1)f_{s,v+1,r-1} - vf_{s,v,r}\big]\Big] = \\
& \quad = 2k_i[M_2][I] + k_i[I]\Big[\sum_{(0,0,0)}^{\infty} s(v+1)f_{s,v+1,r-1} - \sum_{(0,0,0)}^{\infty} svf_{s,v,r}\Big] \\
& \quad = 2k_i[M_2][I] + k_i[I]\Big[\sum_{(0,1,-1)}^{\infty} svf_{s,v,r} - \sum_{(0,0,0)}^{\infty} svf_{s,v,r}\Big] \\
& \quad = 2k_i[M_2][I].
\end{aligned} \tag{27}$$

2. Propagation

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} 2srk_p[M_2](f_{s-1,v-1,r} - f_{s,v,r}) = \\
&= 2k_p[M_2]\Big[\sum_{(0,0,0)}^{\infty} srf_{s-1,v-1,r} - \sum_{(0,0,0)}^{\infty} srf_{s,v,r}\Big] = \\
&= 2k_p[M_2]\Big[\sum_{(-1,-1,0)}^{\infty} (s+1)rf_{s,v,r} - \sum_{(0,0,0)}^{\infty} srf_{s,v,r}\Big] = \\
&= 2k_p[M_2]c_r.
\end{aligned} \tag{28}$$

3. Crosslinking

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} sk_p\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r)} r'(v-v'+1)f_{s',v',r'}f_{s-s',v-v'+1,r-r'} - (c_r v + c_v r)f_{s,v,r}\Big] = \\
&= \sum_{(0,0,0)}^{\infty} sk_p\Big[\Big(rf_{s,v,r} * (v+1)f_{s,v+1,r}\Big) - (c_r v + c_v r)f_{s,v,r}\Big] \\
&= \sum_{(0,0,0)}^{\infty} sk_p\Big[T_{010}\Big(rf_{s,v,r} * vf_{s,v,r}\Big) - (c_r v + c_v r)f_{s,v,r}\Big], \\
&= k_p\Big[x\big(\frac{1}{y}(zF_z yF_y)\big)_x - x\big(F_z(1,1,1)yF_y + F_y(1,1,1)zF_z\big)_x\Big]\Big|_{x=y=z=1} = \\
&= k_p\Big[\frac{1}{y}x(zF_{zx}F_y + zF_z yF_{yx}) - x\big(F_z(1,1,1)yF_{yx} + F_y(1,1,1)zF_{zx}\big)\Big]\Big|_{x=y=z=1} \\
&= k_p\Big[\Big(F_{zx}(1,1,1)F_y(1,1,1) + F_z(1,1,1)F_{yx}(1,1,1)\Big) \\
&\quad - \Big(F_z(1,1,1)F_{yx}(1,1,1) + F_y(1,1,1)F_{zx}(1,1,1)\Big)\Big] \\
&= 0.
\end{aligned} \tag{29}$$

4. Termination by disproportionation

$$\begin{aligned}
&\sum_{(s,v,r)=(0,0,0)}^{\infty} 2sk_{td}c_r\Big((r+1)f_{s,v,r+1} - rf_{s,v,r}\Big) = \\
&= 2k_{td}c_r\Big[\sum_{(0,0,0)}^{\infty} s(r+1)f_{s,v,r+1} - \sum_{(0,0,0)}^{\infty} srf_{s,v,r}\Big] \\
&= 2k_{td}c_r\Big[\sum_{(0,0,1)}^{\infty} srf_{s,v,r} - \sum_{(0,0,0)}^{\infty} srf_{s,v,r}\Big] = 0.
\end{aligned} \tag{30}$$

5. Termination by recombination

$$
\begin{aligned}
\sum_{(s,v,r)=(0,0,0)}^{\infty} sk_{tc}\Big[\sum_{(s',v',r')=(1,0,1)}^{(s-1,v,r+1)} r'(r-r'+2)f_{s',v',r'}f_{s-s',v-v',r-r'+2} - c_r r f_{s,v,r}\Big] = \\
&= \sum_{(s,v,r)=(0,0,0)}^{\infty} sk_{tc}\Big[\Big((r+1)f_{s,v,r+1} * (r+1)f_{s,v,r+1}\Big) - 2c_r r f_{s,v,r}\Big] \\
&= k_{tc} \sum_{(s,v,r)=(0,0,0)}^{\infty} \Big[sT_{002}(rf_{s,v,r} * rf_{s,v,r}) - 2c_r s r f_{s,v,r}\Big] \\
&= k_{tc}\Big[x\Big(\frac{1}{z^2}(zF_z zF_z)\Big)_x - 2F_z(1,1,1)x(zF_z)_x\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[x(F_z^2)_x - 2F_z(1,1,1)xzF_{zx}\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[2xF_{zx}F_z - 2xzF_z(1,1,1)F_{zx}\Big]|_{x=y=z=1} \\
&= k_{tc}\Big[2F_{zx}(1,1,1)F_z(1,1,1) - 2F_z(1,1,1)F_{zx}(1,1,1)\Big] = 0.
\end{aligned}
\tag{31}
$$

The PBE for the concentration of reacted monomer units, calculated by summing up all five contributing terms, results in

$$
\dot{c}_s = 2k_i[M_2][I] + 2k_p[M_2]c_r. \tag{32}
$$

The PBE for the concentration of crosslinks are obtained by

$$
\begin{aligned}
\dot{c}_c &= \dot{c}_s - \dot{c}_v \\
&= 2k_i[M_2][I] + 2k_p[M_2]c_r - \Big(k_i(2[M_2]-c_v)[I] + 2k_p[M_2]c_r - k_p c_r c_v\Big) \\
&= k_i c_v[I] + k_p c_r c_v,
\end{aligned}
\tag{33}
$$

and the PBE for the concentration of reacted monomers reads

$$
[\dot{M}_2] = -\dot{c}_s = -2k_i[M_2][I] - 2k_p[M_2]c_r. \tag{34}
$$